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Proposed Combined Sewer Control by Electrode Potential

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PROPOSED COMBINED SEWER CONTROL
BY
ELECTRODE POTENTIAL

FEDERAL WATER QUALITY ADMINISTRATION
DEPARTMENT OF THE INTERIOR

by

Merrimack College
North Andover, Massachusetts

Contract No. 217-01-68
11024 DOK
FEBRUARY, 1970

FWPCA Review Notice

This report has been reviewed by the Federal Water Pollution Control Administration and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Federal Water Pollution Control Administration.

ABSTRACT

The objective of the project was to investigate the effectiveness of electrode potential measurements to modulate discharges from combined and storm sewer overflows to reduce stream and estuarine pollution. Studies included varying the composition of sewage, flow rate and examining the tendency to polarize or coat the electrodes under actual flow conditions. The analysis of experimental results shows a high degree of correlation between the electrode potential of the sewage and its strength. Linear correlation coefficients between electrode potential and the various sewage parameters measured were found to be as shown below:

Parameter	Linear Correlation Coefficient
BOD	0.873
COD	0.852
Sulfides	0.896
Total Phosphorus	0.893
Nitrates	0.807
Chlorides	0.225

These results were obtained using predominantly stale, domestic sewage in the laboratory and more work should be performed with fresh sewage to substantiate these findings. This work should be supplemented by a field demonstration.

The 3/8-in. diameter Ag, AgCl-Pt flow-through cells were found to yield the most stable, reproducible and accurate readings. It was found that immersion electrodes do polarize while the Ag, AgCl-Pt flow-through cell has shown no polarization during the ten months of sewage experimentation. The response time was instantaneous when flow through the cell was changed from tap water, or the standard ferricyanide-ferrocyanide solution, to sewage.

It was found that the potential measures positive or small negative values when DO levels are above 1 mg/l and drops sharply to measure highly negative values when DO concentrations fall below 1 mg/l.

In the examination of the effect of flow rate on the electrode potential, little, if any, effect was noticed when the flow rate was varied from 0.5 liter/minute to 4 liter/minute. The effect of very high and very low flow-through velocities should be investigated.

Based on these limited investigations it appears that the addition of a buffer to sewage may be helpful in stabilizing the potential, although the influence of a strong reductant may be masked.

It was demonstrated that the potential will be more negative the greater the $S^=$ concentration, except when a small amount of DO is present which exerts an attenuating influence. Flows carrying substantial concentrations of reducing substances with a detrimental impact on the dissolved oxygen reservoir of any receiving waters must be kept from exerting their damaging influence on bathing beaches, tidal estuaries and other water resources. Controlling the flow from outfalls by the electrode potential should significantly help to minimize such insults to the environment.

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IV. CONCLUSIONS AND SUMMARY

1. The average annual overflow from sewerage systems is estimated to contain 3 to 5% of the untreated sewage and during storms, as much as 95% of untreated sewage. Stormwater and combined sewer overflows are responsible for major amounts of polluting material in the Nation's receiving waters. Urban runoff and agricultural drainage contribute significant amounts of pollutional materials to watercourses. These discharges affect all known water uses adversely.

2. The 3/8-in. diameter Ag, AgCl-Pt flow-through cells were found to yield the most stable, reproducible and accurate readings. It was found that immersion electrodes do polarize while the Ag, AgCl-Pt flow-through cell has shown no polarization during the ten months of sewage experimentation. The response time was instantaneous when flow through the cell was changed from tap water, or the standard ferricyanide-ferrocyanide solution, to sewage.

3. In the laboratory, the stationary electrodes polarized when immersed in sewage at 20°C for a period of seven days, but under the same conditions a similar problem did not arise using the flow-through type cell. Potential measurements in sewage using the flow-through type cell can be obtained with a reproducibility within 1 or 2 millivolts.

4. The response of the cell has been instantaneous when changing the substrate flowing through it from water (+300 mv) to stale sewage (-250 mv) at 20° or 25°C. Potential changes in the sewage itself, by the addition of sulfide ion or aeration have been recorded instantaneously also, indicating the sensitivity of the cell to changes in the substrate.

5. The analysis of experimental results shows a high degree of correlation between the electrode potential of the sewage and its strength. Linear correlation coefficients between electrode potential and the various sewage parameters measured were found to be as shown below:

Parameter	Linear Correlation Coefficient
BOD	0.873
COD	0.852
Sulfides	0.896
Total Phosphorus	0.893
Nitrates	0.807
Chlorides	0.225

These results were obtained using predominantly stale, domestic sewage in the laboratory and more work should be performed with fresh sewage to substantiate these findings. This work should be supplemented by a field demonstration.

6. Automatic records of the potential demonstrate that continuous potential recording can be achieved successfully. The response and sensitivity of the sensing cell have been investigated.

7. The proposed system, if measuring a potential falling to -30 mv or below (signalling facultative anaerobic waste characteristics with potentially damaging effects on the receiving waters), would trigger a solenoid which by telemetering would close a gate in the outfall. Thus, the flow will be shunted to a pond or tank until the potential rises to +25 mv or +30 mv indicating satisfactory characteristics to permit direct release to the stream.

8. It was found that the potential measures positive or small negative values when DO levels are above 1 mg/l and drops sharply to measure highly negative values when DO concentrations fall below 1 mg/l.

9. In the examination of the effect of flow rate on the electrode potential, little, if any, effect was noticed when the flow rate was varied from 0.5 liter/minute to 4 liter/minute. The effect of very high and very low flow-through velocities should be investigated.

10. Based on these limited investigations it appears that the addition of a buffer to sewage may be helpful in stabilizing the potential, although the influence of a strong reductant may be masked.

11. From controlled laboratory investigations, the results of which are seen in Table VIII, it is known that formation of sulfides will start to depress the potential, especially after the DO in the system has been exhausted.

12. It was demonstrated that the potential will be more negative the greater the $S^=$ concentration, except when a small amount of DO is present which exerts an attenuating influence. Flows carrying substantial concentrations of reducing substances with a detrimental impact on the dissolved oxygen reservoir of any receiving waters must be kept from exerting their damaging influence on bathing beaches, tidal estuaries and other water resources. Controlling the flow from outfalls by the electrode potential should significantly help to minimize such insults to the environment.

In summary, the following additional comments may be helpful:

Although it is recognized that overflow discharges are not necessarily anaerobic, the flows most detrimental to the oxygen balance of any receiving waters contain reducing substances in substantial concentration. Much of the laboratory work was carried out with stale sewage to similate similar conditions, especially the production of sulfides - long a problem in large sewerage systems and long outfall lines.

Without wanting to imply that the data from these studies are adequate to set any operating standards, some preliminary estimates for an operational potential are possible. For the present, an operating level of electrode potential of at least +25 or +30 appears to be a potential level above which the oxygen balance in any receiving water would not be damaged. Therefore, discharges much below this potential should not be tolerated.

In the examination of the effect of flow rate on the electrode potential little, if any, effect was noticed when the flow rate was varied from 0.5 liter/minute to 4 liter/minute. The effect of very high and very low flow-through velocities should be investigated.

The mv signal may have to be integrated with a definite time constant to be determined in each case.

Application of the electrode potential control for the intermittant flows from combined sewer overflows and storm sewers promises to be an economical solution as part of the overall pollution abatement program facing this Nation's rivers and shorelines. Controlling the flow of combined sewer and stormwater outfalls by the electrode potential should definitely help to minimize such insults to the environment.

As water quality requirements or standards change or are upgraded, the critical potential level can be adjusted readily. This intrinsic flexibility demonstrates a further advantage of the potential method as compared with fixed treatment plant capacity or other devices.

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V. RECOMMENDATIONS

1. The degree of correlation achieved between the potential and standard parameters, such as BOD, COD, sulfides, total phosphorous and nitrate nitrogen, provides a meaningful basis for demonstration of the laboratory calibrated electrode system. Following additional analysis of the laboratory model with more dilute combined sewage and stormwater, pilot studies, including field testing of the electrode system in an existing outfall, are still needed to substantiate laboratory findings. During the first year of this study it was demonstrated that a stable and significant potential response by the electrode system for untreated sewage can be obtained and that continuous potential recording can be achieved successfully. Additional data of the type obtained is necessary to strengthen and substantiate the present conclusions.

2. Although the effect of strong reducing substances in the form of sulfides have been investigated, additional studies should be conducted to establish the effect of other reductants, if any, present in sewerage systems before flow modulation by potential is practiced. Longer periods of contact with substrates containing a high concentration of sulfides should be investigated to examine the effect of these substances on the electrodes.

3. A limited study of the effect of phosphate buffer to improve the poising of the substrate medium was undertaken. Based on these limited investigations it appears that the addition of a phosphate buffer to sewage may be helpful in stabilizing the potential, under certain conditions. Further laboratory work, including extension to other buffer systems, is needed.

4. The effect of the flow-through velocity on the electrode potential signal from flow-through type cell systems, especially at very low and high velocities, is still not entirely clear. Although no appreciable affecton the potential was found with flow rates varying from 500 ml/min to 4,000 ml/min, a wider range of flow rates should be explored.

5. The effect of temperature and the response of the potential measuring system under widely varying sewage strengths (dilute storm sewage) should be further investigated.

6. Following the significant correlation obtained in these studies between electrode potential and total phosphorous concentration ($r = 0.89$) and nitrate nitrogen ($r = -0.81$), the applicability of the electrode potential to determine discharges of urban runoff and agricultural drainage qualities should be investigated. Wastewaters containing urban runoff and agricultural drainage type pollutants, high in nutrients, may be prepared synthetically in the laboratory and the response, sensitivity and stability of the electrode potential to these wastewater characteristics established before a field demonstration is undertaken.

7. The potential cell developed by Universal Interloc, Inc., claimed to have improved characteristics, should be investigated along with the Fischer and Porter system which has given the most stable, reproducible and accurate readings. The latter showed especially desirable long-term stability in the laboratory with a range of untreated sewages, including concentrations of sulfides up to 30 ppm. This electrode system should be investigated in an existing outfall, unless the Universal Interloc sensor proves to be a superior system.

8. A conceptual design of a prototype installation to control the quality of discharge from a combined or storm sewer was shown in Figure 4. The mv signal was shown as simply transmitted to a potential recorder. The telemetering of an amplified signal to actuate a solenoid-operated valve should be investigated in an actual field investigation. The instantaneous changes in wastewater quality in combined and storm sewers may produce highly variable potentials. Therefore, the millivolt signal may have to be integrated with a time constant to be employed as a control.

VI. INTRODUCTION

A. Scope of Problem

The problems associated with storm sewers, combined sewers and overflows therefrom discharging drainage and wastewater into the Nation's water resources have been found to produce uniformly adverse effects. Wastewater and storm drainage reaching receiving streams without treatment originate from combined sewer overflows directly to streams and tidal basins. Stormwater drains also discharge directly to streams, and bypasses of wastewater from treatment plants and pumping stations, usually occurring during storms, represent additional uncontrolled discharges to watercourses.

Since the first flush of storm water is likely to move most of the accumulated sewer deposits, its interception is particularly important. In the case of intercepting sewers, most of the storm water carried by the collector tributary to the interceptor must be allowed to overflow into the receiving body of water that the interceptor is designed to protect. This overflow contains a proportionate share of the sanitary sewage that enters the combined system during the period of storm runoff. As a result, the total amount of polluting material reaching the "protected" body of water in the course of a year is usually a significant though small fraction of the total annual volume of sanitary sewage. The annual average overflow is estimated to contain 3 to 5 percent of the untreated sewage and, during storms, as much as 95 percent of untreated sewage (1).

The quality of the overflows reflects a high degree of pollutional load to watercourses as measured by the usual standards of biochemical oxygen demand, coliform organisms, solids, etc. For example, data from Buffalo, N.Y. indicate that about one-third of the city's annual production of sewage solids overflowed without treatment, although only 2 to 3% of the sewage volume actually overflowed. More important is the danger to public health from the pathogenic bacteria and viruses that are present in raw sewage. Stormwater alone was demonstrated to carry significant amounts of pollutional load, particularly in the early portions of storms when a flushing action occurs. This phenomenon is responsible for substantial organic loading of streams during storms. All types of water uses are affected. The problem is of major importance and is growing worse with increasing urbanization and water demands.

In view of the seriousness of the problem a preliminary evaluation of the effectiveness of the electrode potential as a measure of strength of pollutant, and ultimately as a control device, has been needed. The activity of the system establishes a potential range which may be used to modulate the flow into a receiving stream, lake or tidal basin, or to a holding tank or pond until the effluent quality improves. While the electrode potential is not related directly to the dissolved oxygen concentration, it is a measure of the relative concentrations of overall oxidants to reductants.

In November 1965 the White House released a report (2) "Restoring the Quality of Our Environment", which points out that "two-thirds of the U. S. population, about 125 million people, are served by domestic sewers." Sewage from about one-tenth of these people is discharged raw. Furthermore, stormwater from heavy rains exceeds the capacity of existing treatment plants in communities with combined sewers, resulting in considerable amounts of sewage being discharged raw. In total, sewage discharges correspond to the raw sewage from almost 50 million people (2).

In Massachusetts alone, there are 37 cities and towns that are served exclusively by combined sewers, serving a population of almost one million (0.95 million). In the U. S. there are some 125 million people served by combined or separate sanitary sewer systems (2)(3), The 59 million people affected by the combined sewer systems represent 50 percent of the total sewered population (1). A 1967 survey conducted by the APWA for FWPCA (3) estimated that there are 1,329 jurisdictions, served in whole or in part by combined sewers, having a total population of 54 million. The cost for replacing the combined sewers with separate sanitary and storm sewers was estimated to be approximately $30 billion. To effect total separation, including expenses necessary for plumbing changes, would increase this cost to approximately $48 billion. The report discloses that the possibility of changing all combined sewers to separate is remote. Therefore, a more economical solution, such as the interception of the first surge containing most of the accumulated sewer deposits, by the electrode potential method, was suggested by the principal investigator and studied during the past year. The results of this study form the body of this report.

(a) Characteristics of Combined and Stormwater Flows:

Various investigators (4) (5) (6) (7) have estimated the proportion of sewage that is diverted to a receiving body of water through overflow structures for various capacities of the interceptor sewer. Intercepting sewers generally allow for the collection of the maximum dry-weather flow and the first surge of storm flow for treatment. Where rainfalls are intense and of short duration, as in most parts of the North American continent, it is not possible to discharge a substantial amount of stormwater through interceptors that are reasonably proportioned. Thus, interceptors are commonly designed to carry only two or three times the average dry-weather flow, or from 250 to 600 gpcd. A more informative measure of the capacity of interceptors in excess of the average dry-weather flow is the amount of rainfall or runoff that they can carry, expressed in inches per hour. In 1947 McKee (4) studying overflows from combined sewers in Boston, Massachusetts, found that when flow in sewers is twice the average dry-weather flow, approximately 2.7% of the total annual flow of domestic sewage may be expected to overflow to the receiving stream. The basic data were developed for low intensity, prolonged rains but were projected to include high intensity storms. During storms the percentage of sewage lost by overflow would be quite high. Thus, for a rainfall intensity of only 0.1 in/hr, it was found that 82% of the sewage during the storm would overflow from a system designed for twice the dry-weather flow, and 73% would overflow if the system were designed for three times the dry-weather flow. For storms of 0.5 in/hr, the overflow would be 97 and 94%, respectively. Even with interceptors designed to collect up to 9 times the dry-weather flow, 82% of the sewage would overflow from storms of 0.5 in/hr. Thus, even with relatively small rainfall intensities "significant pollution in terms of organic load and bacterial contamination will be discharged directly into the watercourse" (4).

Similarly, Shifrin and Horner (5) in St. Louis found the sewage discharged by combined sewer overflows to vary from 2.2% to 3.1% of total annual flow; while Moorhead (6) estimated for Washington, D.C. an annual average of 3.3% or 3.6 mgd of sewage, lost by overflows from combined sewers.

In many areas the frequency of storms causing significant discharges of sewage to the streams is far too high for adequate protection of the receiving water. For interceptors designed for 1.5 to 3 times average dry-weather flow, McKee (4) found that overflows may be expected 5 to 6 times per month in the summer; much too frequent for waters to be used for bathing or shellfish propagation. Johnson (8) showed that at several outflow points in Washington, D. C. the average number of overflows varied from 5 to 17 per month in the summer and from 3.8 to 4.7 per month in the winter. Agreeing with these findings are the results of studies made for New York City (9), Kansas City, Mo. (10) and Northampton, England (11). A more recent survey (3) indicates that for the 14,212 overflow points examined, overflows occur an average of 28 times per year and each overflow event lasts for an average of five hours.

(b) Quantity of Combined Overflows and Stormwater:

Complete information is not available on the quantity of discharge from overflows because the complexities inherent in any collection system. Accepting that from 3 to 5% of untreated wastewater annually reaches watercourses from combined sewer overflows and confining the estimate to the conservative side of the range at 3% annual overflow, almost 60 billion gallons of raw sewage per year enter the rivers, streams and tidal estuaries of this Nation (1). This amounts to about 200 tons of BOD per day. Enormous quantities of stormwater of questionable quality must be added to these figures.

Quantities of stormwater alone discharged by sewers vary greatly in different areas, depending on the rainfall - runoff pattern. However, with a few assumptions, an estimate of the amounts of surface runoff from storms may be obtained. If it is assumed that 1/3 of the total area is impervious for an urban community served by sewers, the runoff volume will amount to 5.8 mg/sq.mi. per inch of rainfall. There are some 11,400 communities of all sizes in the 50 States, having a total area of 43,000 sq.mi. Applying the above criteria, total stormwater runoff will equal 25 BG for each inch of rainfall. Chicago, with 190 sq.mi. of sewered area serving 3.5 million people, under these assumptions, produces a stormwater runoff of 1.1 BG per inch of rain.

(c) Damages Due to Stormwater:

The most frequent problem arises from the surcharge of sewers, flooding residence and business basements with a combination of untreated sewage and stormwater. Besides causing a nuisance, it represents a financial loss and is also a menace to public health. Preliminary results of a study of the flow and composition of stormwater at three stations in Northamption, England, suggest that stormwater overflows differ in character from what might be expected. It was expected that the results would show a heavy runoff to dilute the sewage, thus creating little pollution. Instead, the suspended solids concentration increased as the intensity of runoff increased. With storm flow 3 times that of dry-weather flow, samples taken in the first five minutes at one station showed that average suspended solids concentration was 250% of that found in the sewage. However, samples taken more than 35 minutes later dropped to a 75% concentration. The British studies also showed that large deposits of solids accumulated in large, old sewers, especially those with relatively flat slopes. Apparently, deposits build up in dry weather and high flows during rainstorms pick them up to produce the high solids concentration.

(d) Effect on Streams from Wastewater Overflows:

Despite essentially separate collection system, wastewater flows in interceptors increase substantially during storms. It is not known exactly how the stormwater reaches the interceptors, but it is presumed that rising groundwater (infiltration) and flow from connected roof leaders, catchbasins, basement sumps, and yard drains all contribute. Because the treatment plant will not accommodate the increased hydraulic load, it is necessary to bypass the plant during storms. For example, stormwater-diluted wastewater is bypassed through outfalls to San Francisco Bay from the East Bay Metropolitan Utility District.

Another way of measuring the effect of stormwaters on watercourses is by examining conditions at pumping stations when it is necessary to bypass during storms. Table I presents stream quality data showing the effect of bypass discharges from pumping stations. Samples were taken upstream and downstream from, and at, the station. At the same time samples were taken from a nearby stream which did not receive wastewater overflows. The organic and bacteriological quality of the water upstream from the discharge point is about equivalent to the stream not receiving waste; however, the inorganic load imposed by erosion into the creek is apparent in the concentrations of solids. The harmful effect on the stream by the wastewater is clearly demonstrated in Table I by the increase in B.O.D. and coliform counts.

TABLE I

Stream Quality Conditions at Time of Bypassing Pumping Stations

Determination	Upstream		Point of Discharge		Downstream		Another Stream Not Receiving Discharge	
	Avg.	Max.	Avg.	Max.	Avg.	Max.	Avg.	Max.
BOD (mg/ml)	6.8	21	92	360	25	60	9.5	16
T. S. (mg/ml)	469	748	385	543	918	2,482	6,026	6,672
Coliform (MPN/ 100 ml)	1,990	4,250	48,200	70,000	40,500	126,500	2,435	4,250

Generally accepted engineering practice in this country has been to design combined sewers to handle during storms two to three times the dry weather flow. Bypassing the excess directly to the nearest watercourse is accomplished by any of several schemes. The surcharging and overflowing of combined sewers is more objectionable than the backing up of drains that carry only storm water. The amount of water entering at the junctions of the submains in a combined system must be controlled by admitting only as much water to the interceptor as its capacity permits. All water in excess of this value must be diverted into stormwater overflows. This diversion can be regulated hydraulically or mechanically. There are many hydraulic separation divices, such as the side overflow spillway weir, leaping (gap) weir, siphon spillway, perpendicular weir (diversion dam), tipping-gate regulator and orifice or drop-inlet regulator. Mechanical diversion of storm-water flows is generally regulated by a float-operated valve which controls the admission of water to the interceptor, such as the float-operated gate, hydraulic cylinder, manual or automatic valve which may require changing of position if a slide or sluice gate type of valve is used. All types of regulators share one common difficulty - they present operating and maintenance problems without which they are prone to clogging.

It is established that the overflows from combined sewer systems and the discharge of stormwater from storm sewers contribute directly to pollution. As mentioned earlier, the high cost of sewer separation plus the very significant possible need for separate treatment of stormwater has been the subject of a recent study (12). Information on combined sewer service was obtained by direct inverviews of 641 jurisdictions having a total population of 51 million. Projected to the entire Nation, it was estimated that there are 1,329 jurisdictions, served in whole or in part by combined sewer systems, including plumbing, could cost approximately $48 billion. Therefore, electrode potential control for these intermittant flows promises to be a more economical solution as part of the overall pollution abatement program of this Nation's rivers and shorelines.

B. Overall Purpose of Project

The purpose of this project has been to initiate an investigation of the effectiveness of electrode potential control to regulate the flow of untreated sewage and waste effluents to protect the water quality of receiving streams and tidal basins. Pollution abatement from these wastewaters may be achieved by diversion of discharges (such as: bypasses of wastewater by treatment plants and pumping stations and the flushing of accumulated organic matter during the early flooding from stormwater) to holding tanks, ponds and/or subsequent exposure to waste treatment.

Sewer systems with overflows contribute materially to pollution and particularly during storms. The annual average overflow was estimated to contain 3 to 5 percent of the untreated sewage and, during storms, as much as 95 percent of untreated sewage. Stormwater quantities are in addition to these amounts. These overflows contribute a high degree of pollutional load to watercourses as measured by biochemical oxygen demand, coliform organisms, solids, etc. Stormwater alone has been demonstrated to carry significant amounts of pollution (see Chapter VII, Section 7), especially during the early part of storms when a flushing action occurs.

Rather than the entire overflow discharging into a river or estuary, the ultimate objective of electrode potential control is to program the amount of overflow held back (especially the early slugs) for additional treatment. The electrode potential system will sense the effluent quality and relay the signal to a flow regulator. As the quality of the discharge improves, the flow will be sent to the stream. This modulation according to quality leads to smaller sized holding ponds or tanks and thus reduces the construction cost of the hydraulic structure. Therefore, control by the electrode potential method will be able to modulate overflows from combined systems to intercept discharges to a receiving stream or other watercourse that would otherwise contribute materially to their pollution. Diverting flows of this nature to a minimum sized pond or tank permits subsequent treatment to any desired degree to be achieved. By containment of the most offensive and strongest discharge surge, only a relatively small treatment volume is necessary. Most important, the water quality of the receiving stream or estuary will be safeguarded automatically and continuously.

Following the analysis of the electrode system in the laboratory during the first year, pilot studies, including field testing and demonstration of the laboratory model in one or more outfalls should be undertaken to substantiate laboratory findings during the second year.

C. General Background

1. Plan of Operation

The project plan has been basically a research phase leading to a pilot plant demonstration. The first phase, underway since March 1969, has been carried out in the laboratory. It consisted of measuring electrode potentials of untreated or partially treated wastes with which to modulate the flow. Several electrode systems, their stability, response and reliability have been investigated and compared. The most reliable electrode system can be incorporated in an electrolytic control circuit for control of the effluent quality. Provided the project is continued, the second year will be devoted to testing the calibrated electrode system by operating this model under field conditions to evaluate its response to meet water quality standards.

2. Objectives

The immediate objective of this study has been to investigate the response and the effectiveness of the electrode potential as a measure of the strength of wastewater discharges from combined sewer overflows and storm sewers. Further work is expected to demonstrate the control of harmful discharges by the electrode potential method. In practice, the potential will be used to modulate the discharge (especially the early flushings) from combined and storm sewers by temporarily diverting this flow until it can receive adequate treatment, following the period of peak flow through the treatment plant.

A measured potential falling to say -30 mv (signalling a polluted effluent with potentially damaging effects on the receiving waters) triggers a solenoid which by telemetering will close a gate in the outfall. Thus, the flow will be shunted to a pond or tank until the potential rises to say +25 mv or +30 mv, indicating satisfactory characteristics to permit release to the receiving stream. The mv signal may have to be integrated with a definite time constant to be determined in each case.

The proposed system has been investigated initially for effectiveness of response to a variety of sewage strengths by the operation of a laboratory test model. These studies have included: 1) varying the composition of sewage (synthetic and real sewage), 2) varying the degree of aeration, 3) varying the concentration of sulfides, 4) examining the presence of grease, 5) varying the flow rate, 6) examining the tendency to polarize or coat the electrodes under actual flow conditions, and 7) investigating the effect of different cell systems on the response. Following the analysis of this model in the laboratory, pilot studies, including field testing of the electrode system in an existing outfall, are necessary to substantiate laboratory findings.

3. Redox Potential Fundamentals

Many of the chemical and biochemical processes encountered in sewage and industrial wastes can be described fundamentally as oxidation-reduction systems. Although determination of the electrode potential does not itself explain the nature of the systems at work, it is used to evaluate the magnitude and character of process changes. Measurement of a redox potential has been facilitated considerably in recent years due to improvements in potentiometers and metallic electrodes which have resulted in greater accuracy and convenience. The development of the flow-through cell system may be regarded as a definite "breakthrough", virtually eliminating polarization of the electrodes.

According to the definition of the oxidation-reduction process, oxidation involves a loss, and reduction, a gain, of one or more electrons. A typical example is the hydrogen electrode, where the hydrogen gas is the reduced and the hydrogen ion is the oxidized form.

The redox potential is a measure of the tendency for a substance to give up or to accept electrons. It is a quantitative measure of the free energy of the reaction (or myriads of reactions) involved in the electronic transfer. During the metabolic process of microorganisms, a definite oxidation-potential is maintained in a particular organism-substrate system, the reduction intensity of which depends on the species, cultural age, its variation phase, and its environment (13). The value of redox potentials in characterizing a physiological state in higher forms of life has been established. The relationships between reduction intensity and known physiological conditions have already proven of special value in bacteriology.

Transfer of an electron or electrons from one compound to another is a result of potential difference between the two reactants. The magnitude of this potential difference depends upon the ease with which the electrons are lost or gained. The greater the oxidizing or reducing power of a substance, the greater will be the electrical potential difference. The oxidation-reduction potential is always referred to the normal hydrogen electrode, assumed to have zero potential. The more highly oxidizing a substance (or bio-system), the more positive will be its electrical potential; the more highly reducing a substance (or bio-system), the more negative will be its electrical potential.

According to Hewitt (13), the Nernst equation as modified by Faraday's law is:

$$E_h = E_o + \frac{RT}{nF} \ln \frac{(\text{Ox.})}{(\text{Red.})} \qquad (1)$$

in which:

E_h = electrode potential with respect to the hydrogen half-cell, (volts);

E_o = a standard potential of the system when the activity of all oxidants and reductants are unity and at 30°C, (volts);

R = 8.315 volt-joules coulombs, (the gas constant);

T = absolute temperature, (°K);

F = 96,500 coulombs, (Faraday's constant);

n = number of electrons participate in the redox potential system.

It is evident from the equation that the greater the relative concentration of oxidized form the higher will be the potential. With a more reduced substance, a lower, or more negative, potential will result. It may be observed that if a system is 50% oxidized, the concentration of oxidants equals that of the reductants, i.e. (Ox.) = (Red.) and $E_h = E_o$. It follows that E_o is a measure of the oxidation and reduction intensity level of the system and enables different systems to be graded in the order of their oxidizing or reducing tendencies. Thus, a system with $E_o = +100$ mv will oxidize a system with $E_o = -100$ mv, but on the other hand, will itself be oxidized by a system with $E_o = +200$ mv, see Figure 1.

Although the measurement of oxidation-reduction potential does not itself explain the nature of the systems at work, the e.m.f. represents their relative proportions. A number of variables affect the potential of a biological system such as sewage and the rate of potential change is a function of: a) kind of organisms present in the substrate; b) condition of organisms; c) growth phase of the microorganisms; d) nature and quantities of other constituents in the system providing environment effects; and e) condition of the process or of the operation.

4. Practical Application of the Potential and Limitations

It is fair to assume that electrode potential instrumentation in the future will be further improved and that present techniques may be compared to the crude hydrogen electrode used at the turn of the century. Nevertheless, potential measurements in sewage can be obtained with a reproducibility within 1 or 2 millivolts.

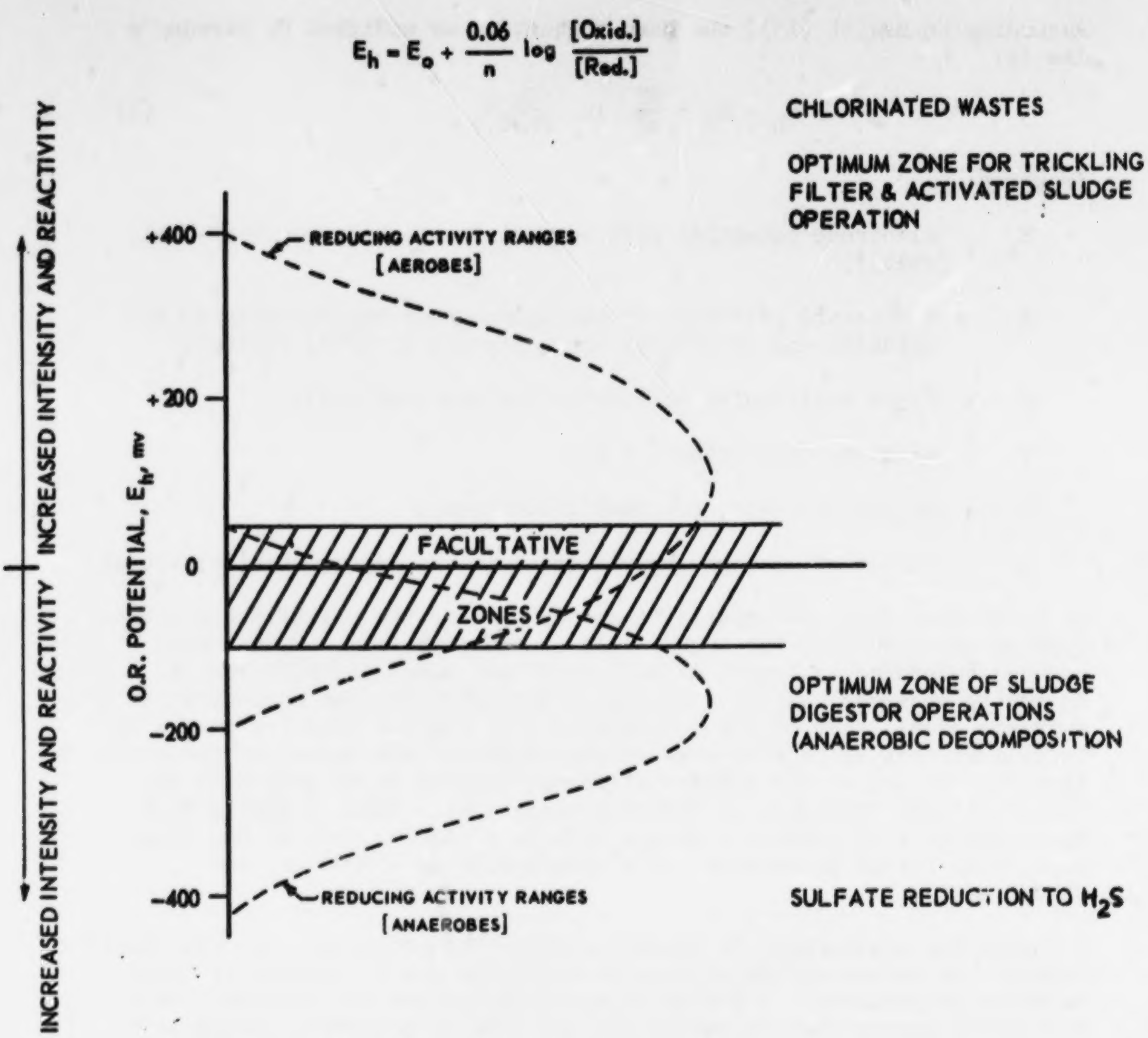

$E_h = E_o + \frac{0.06}{n} \log \frac{[\text{Oxid.}]}{[\text{Red.}]}$
CHLORINATED WASTES
OPTIMUM ZONE FOR TRICKLING FILTER & ACTIVATED SLUDGE OPERATION
INCREASED INTENSITY AND REACTIVITY
INCREASED INTENSITY AND REACTIVITY
O.R. POTENTIAL, E_h, mv
+400
+200
0
-200
-400
REDUCING ACTIVITY RANGES [AEROBES]
FACULTATIVE
ZONES
REDUCING ACTIVITY RANGES [ANAEROBES]
OPTIMUM ZONE OF SLUDGE DIGESTOR OPERATIONS (ANAEROBIC DECOMPOSITION
SULFATE REDUCTION TO H_2S

Figure 1. O.R.P. Relationships in Wastes Treatment

As was recognized by Pomeroy (14): "Determination of the oxidation-reduction potential may provide a quick method of determining the presence or absence of dissolved oxygen or hydrogen sulfide in sewage... and may be a useful analytical method in estimating the degree of contamination of sewage."

The advantage of obtaining an electrode potential of biological systems over most other standard and non-standard parameters to characterize pollution is that it describes the instantaneous state of reaction of the sewage system according to the fundamental electronic concept of matter. Values for other parameters, such as BOD, NO_2-N, NO_3N and other qualitative chemical determinations, yield only the average rate and extent of biological oxidation (15). According to Luck (16), who used redox potential for the determination of chlorine compounds in water, the potential is an analysis that will provide information related to the bactericidal strength of the solution. In chlorination, the electrode potential comes close to attaining this objective because it measures the effective integrated oxidation strength of the materials in a solution - similar to the application in the present studies.

D. Breakdown of Fundamental Operations

1. Chrolology of this Project and Current Status

The original two-year proposal, submitted December 14, 1966, and resubmitted to FWPCA on October 25, 1967, contained a plan of operation which suggested that this research project be conducted in two phases: a) first phase to be carried out in the laboratory and designed to evaluate at the laboratory level the feasibility of measuring electrode potentials of untreated sewage with which to modulate the flow, with the second phase designed to take a calibrated potential system and operating this model under field conditions.

At the time of the official approval by the Commissioner FWPCA, on November 29, 1968, it was clearly stated that the one year project ("to investigate at the laboratory level the feasibility of utilizing electrode potential measuring systems to indicate the strength of combined sewage") is considered as a complete unit although the findings may demonstrate the need for further field projects. The feasibility of the potential method has been clearly demonstrated in the laboratory but additional data are necessary to further substantiate the limits of applicability among untreated combined sewage, domestic sewage, urban runoff, agricultural drainage and industrial waste effluents.

At the time of the official approval, it was further stipulated that: "Subsequent extension into a development field demonstration project shall be submitted as a separate proposal based upon, and justified by, the findings of the feasibility demonstration." A proposal for a Research, Development and Demonstration Contract, dated January 23, 1970, was submitted to FWPCA on January 26, 1970. It proposes essentially the further extension of this project into a field demonstration with continuing laboratory back-up and substantiation of the electrode potential method. The test model should permit in situ study of the effects of film formation, flow rate, temperature variation and permit evaluation of some types of industrial waste admixtures. It is apparent that the complexities and number of variables, viz. intensity and duration of storm, strength of combined sewage or domestic sewage, stream flow regulation, size and slope of sewer, etc. and their interactions will require subjecting automatic electrode potential control to the systems approach. Therefore, the interdisciplinary team approach, as originally proposed and practiced during the current investigations, needs to be continued.

2. Specific Objectives

Specifically, the present studies included the following objectives:

1) to determine the sensitivity of redox potential to the strength of untreated sewage and waste effluents (initially synthetically prepared mixtures),

2) to establish the transient effect of interfering substances or predominant oxidants on the performance of the Potential sensing systems,

3) to investigate the effect of different cell systems on the response and degree of modulation achieved for operating the gate value, or equivalent device.

3. Breakdown into Fundamental Operations

Accordingly, a logical breakdown of the project into its fundamental operations was developed. A schedule of tasks and work effort estimate, as shown in Table II, were submitted to FWPCA on March 14, 1969. Simultaneously, a list of the standard and non-standard sewage parameters was prepared against which the electrode potentials were compared to examine their effect on the electrode, cell system rather than indicating sewage strength characteristics. The list of parameters is shown in Table III. The parameters to indicate the strength of the combined sewage for comparison against potential readings were carefully considered in conference and discussion with Mr. Warren H Oldaker, Project Officer, FWPCA. The usual characterization parameters, including BOD, COD, DO, residue (especially total volatile solids), nitrogenous matter, phosphorous, chlorides, sulfides, pH, temperature and settleable matter were carried out throughout the experimental period and the data are presented later in Table VIII.

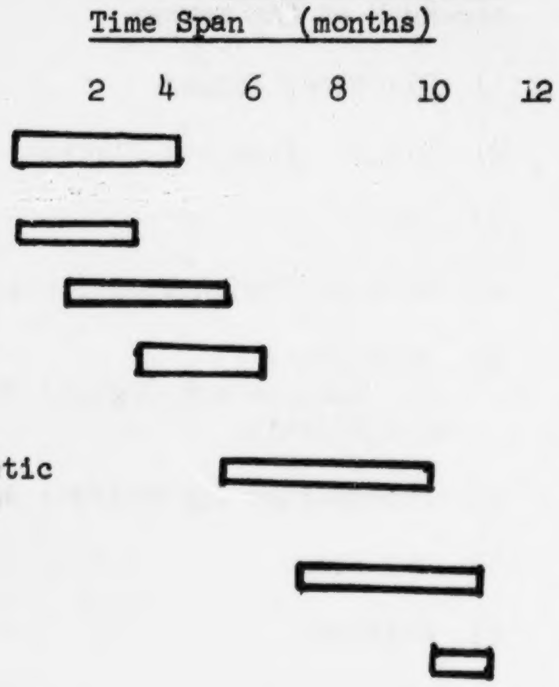
TABLE II

Schedule and Work Effort

A. Schedule. The scheduling of tasks is as follows:

Task

1) Literature Search
2) Ordering of Electrodes and Recorder
3) Setting up Laboratory Experiments
4) Synthetic Sewage and Nutrients Experimentation (Response)
5) Conduct Laboratory Tests with Synthetic and Real Sewage (Collection of Data)
6) Analysis of Data
7) Prepare Final Report



B. Work Effort. The total work effort has been broken down into man-days per task, as shown below:

Task	
1) Literature Search	40
2) Ordering of Electrodes and Recorder	10
3) Setting up Laboratory Experiments	30
4) Synthetic Sewage and Nutrients Experimentation (Response)	50
5) Conduct Laboratory Tests with Synthetic and Real Sewage (Collection of Data)	140
6) Analysis of Data	20
7) Prepare Final Report	30
Total Effort:	320

TABLE III

List of Conventional Sewage Parameters Against Which Potentials are to be Compared

A. Standard Parameters--those involved in the determination of the strength of the sewage:

1) Dissolved Oxygen

2) B.O.D. (two and five-day values)

3) COD

4) Residue (total volatile solids)

5) Nitrogen
    a. Ammonia and Organic Nitrogen (total Kjeldahl)
    b. Nitrate

6) Phosphorous (persulfate digestion)

7) Chloride

8) Sulfides

9) pH

10) Temperature

11) Settleable matter (Imhoff cone)

12) Known redox systems (.01M Borax buffer at pH 9.22 and) (acid potassium phthalate buffer at) (ph = 4.00)

B. Non-Standard Parameters--those involved in determining the proper functioning of the cell system:

1) Ether solubles (polar method)

2) Bacteria (total coliform)

3) Known redox systems (for standardization)

(a) Techniques for Measuring Electrode Potential

Prior to the initiation of experimentation with sewage substrates it was necessary to work out a number of details to determine the response of the potential in the laboratory.

1) Static Measurements: The initial calibrations consisted of immersing standard electrode systems, (Fischer and Porter, Leeds and Northrup, and others) for comparison with known potential systems and were contined throughout the investigations to serve as standard potential measurements; (2) Short Time Duration Measurements: Various sewage substrates and substrate strengths (from fresh to stale effluents) were tested. The purpose of these initial tests was primarily to investigate response, i.e. testing the capability and the speed of the cell to respond to highly variable potentials; 3) Long Time Duration Measurements: During these studies, emphasis was placed on stability of the readings, the effect of electrode polarization, and coating of the electrodes; 4) Short and Long Duration Measurements in Flow-Through Type Cells: The ultimate application was by means of a flow-through cell to overcome the problem of electrode polarization. To examine the validity of the measurements it was necessary to compare frequently the potentials between a static system immersed in a known potential solution, a flow-through cell with the known potential solution circulating through it and a flow-through cell with the substrate being investigates. If any problems would arise, cross-referencing of the potential was possible by interchanging the flow-through cells.

(b) Conditions Necessary to Establish Reliable Potential Readings

To overcome coating of the stationary electrodes, a weak solution of HCl was used for primary cleaning followed by scrubbing with a paste of Alconox powder or Bon-Ami and followed by thorough rinsing with distilled water.

Although a problem not encountered in the laboratory aspects of this work, wetting of the electrodes after prolonged dry periods may be necessary. Wrapping with Mylar, Tedlar, or coating with acrylic sprays may be satisfactory techniques but a loss in sensitivity may result. Application of an aerosol spray may overcome any reduction in sensitivity and should be investigated separately.

Reproducibility of electrode readings, due to a poorly poised system, did not present a problem. Borchardt, at the University of Michigan, found that if the electrodes are allowed to age in the substrate for a 24-hour period, the electrodes give accurate readings, provided the system is free from poisoning. Should the reproducibility of results still pose a problem because of a poorly poised system, it may become necessary to maintain a base level of potential with a phosphate, or borate, etc. buffer system and permit the potential of the substrate to float on the basic buffer potential. Changes in substrate quality would be reflected in a different range of potential level without impairing the usefulness of the potential as a criterion for discharge. (Note: This supposition was developed during the planning stage but the problem never arose during the actual laboratory investigations).

The number of sample specimen taken for analysis was predetermined by deciding that a once per month sampling frequency would permit sufficient time to trace a fresh sewage sample to septicity, and allow for clean-up of equipment and apparatus to get ready for the next run.

The reduction in personnel funds from $26,400 originally requested to the $15,600 granted (a 41% reduction) made it necessary that the number of sewage samples collected and analyses performed be scaled down. Nevertheless, nine (9) major samples (30 gals. each) were collected during the 8-months' experimental period and over 200 analyses were performed, many of these in duplicate and triplicate. Only their averages are shown in the summary tabulation, see Table VIII.

Following discussion of the design and construction of the laboratory demonstration system, the experimental data is presented. The data is discussed with special reference to support the "Specific Objectives".

VII. DESIGN OF LABORATORY DEMONSTRATION SYSTEM AND EXPERIMENTS

To simulate field conditions and to provide the necessary flexibility for experimental purposes, three (3) electrode potential measuring cell systems were employed. One of these was an immersion-type system, used at any time as a reference check of the potential against a known standard potential solution (quinhydrone; Ce(III), Ce(IV); ferricyanide, ferrocyanide system; etc.). The other two electrode systems were identical flow-through cells. One flow-through cell was employed to measure the potential of the actual waste (termed "experimental" cell); the other to make frequent checks against the standard potential solution (termed "control" cell).

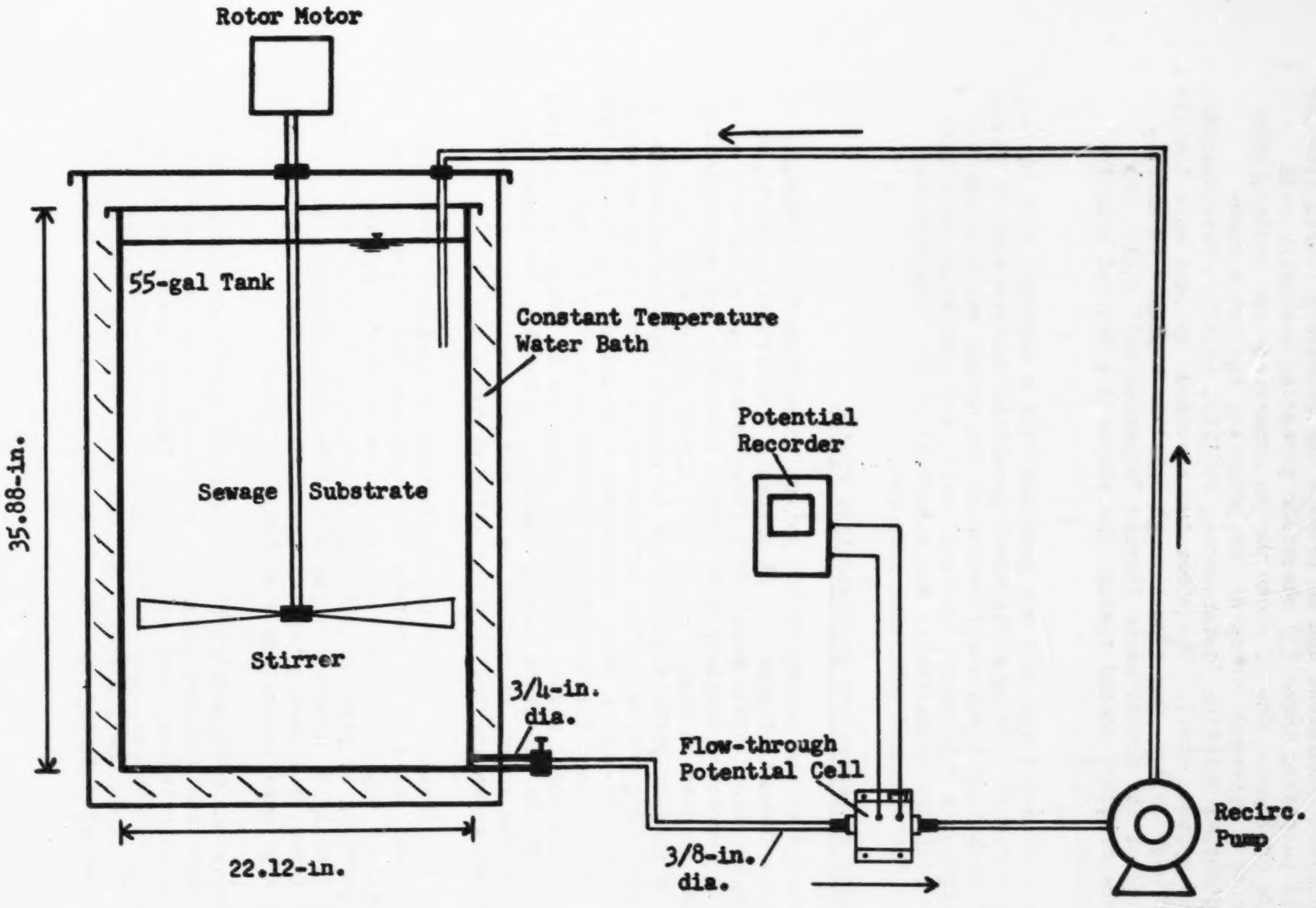
Although each flow-through cell was provided with a separate flow system, a specially designed valving arrangement permitted the reversal of flows, i.e. direct measurement and verification of the actual waste potential by the continuously calibrated "control" cell, and similarly, verification of the response (sensitivity and accuracy) of the "experimental" cell against the standard potential solution.

A. Design of Laboratory Demonstration System

The basic design of the demonstration set-up to perform the laboratory experiments is shown in Figure 2. It presents a descriptive detail of the experimental bench-scale model of a flow-through potential cell and potential recorder, complete with sewage substrate and recirculating pump. As may be seen in Figure 2, it is a closed system with the recirculating pump or peristaltic design to prevent any contamination of the recirculating medium during experimentation. The insulated water bath, made from a 55-gallon drum, surrounded a 30-gallon polyetylene tank with cover and was used for temperature-controlled storage of the substrate. A paddle wheel mixing device was installed to maintain a uniform concentration of the substrate during storage. A Warburg refrigeration bath served as the source of cooling water and the constancy of the water jacket temperature was tested to a variation within ± 0.5°C.

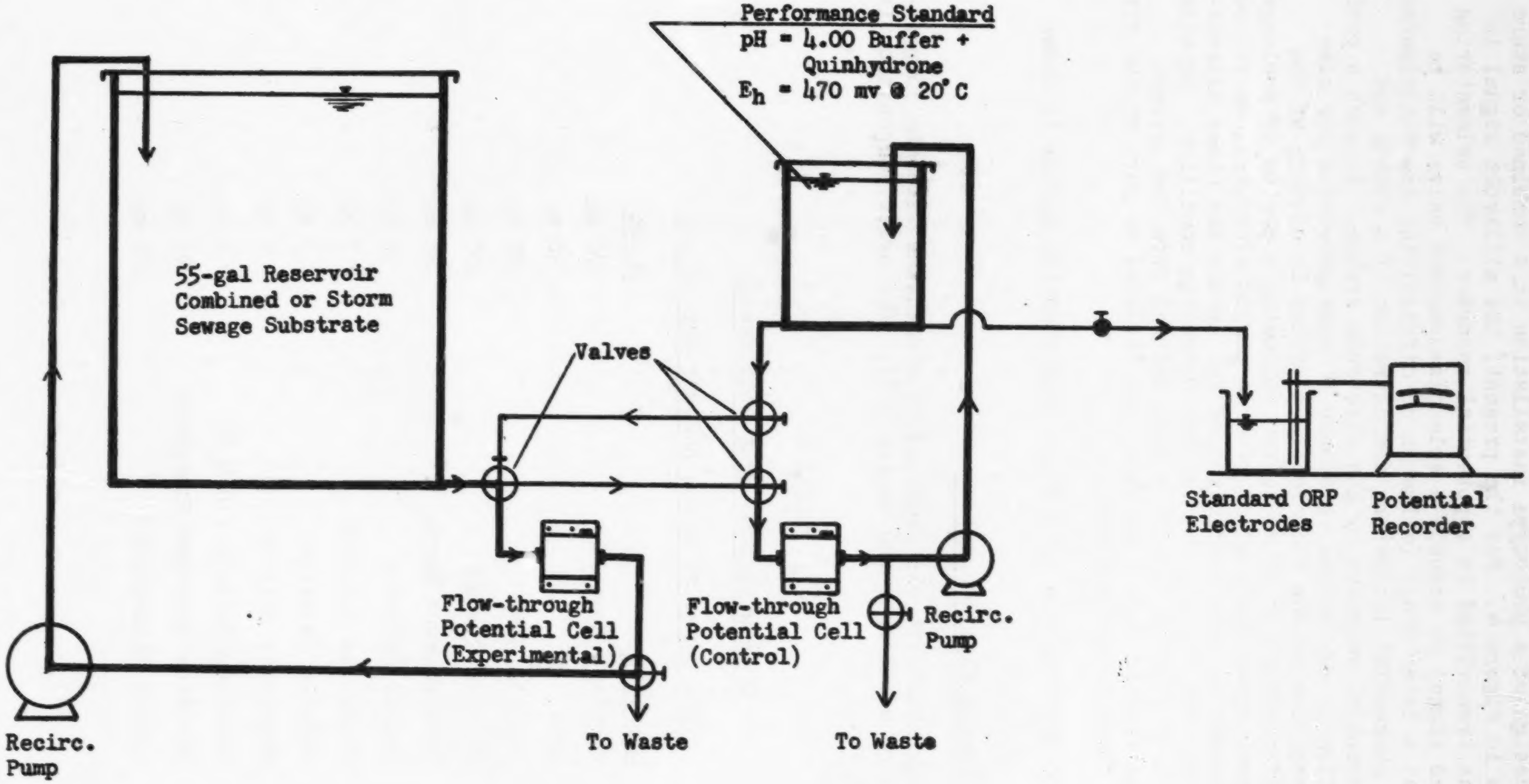
A diagram of the complete laboratory demonstration system is shown in Figure 3. It was designed to operate the "experimental" flow-through potential cell; a separate recirculating system of known standard potential operating in parallel with the identical, "control" electrode system; and finally an immersion-type electrode pair, immersed in a solution of known, standard potential (quinhydrone system or equivalent), to serve as a primary laboratory standard.

Adequate provisions were made to cross-reference electrode systems with sewage substrate and standard potential solutions to check on various operating characteristics, such as electrode fouling, transient effect of interfering substances, predominant oxidants and/or reductants and response of different cell systems, besides verifying the strength of sewage - as needed - during the conduct of the experimental studies.


Rotor Motor
55-gal Tank
Sewage Substrate
Stirrer
Constant Temperature Water Bath
35.88-in.
22.12-in.
3/4-in. dia.
Potential Recorder
Flow-through Potential Cell
3/8-in. dia.
Recirc. Pump

Scale: 1-in. = 10-in.

Figure 2 Detail of Substrate Loop with Electrode Potential Cell


Performance Standard
pH = 4.00 Buffer + Quinhydrone
E_h = 470 mv @ 20°C
55-gal Reservoir Combined or Storm Sewage Substrate
Valves
Flow-through Potential Cell (Experimental)
Flow-through Potential Cell (Control)
Recirc. Pump
Recirc. Pump
To Waste
To Waste
Standard ORP Electrodes
Potential Recorder

Scale: 1-in. = 10-in.

Figure 3 Diagram of Complete Laboratory Demonstration

A conceptual design of a prototype installation in a combined or storm sewer is shown in Figure 4. For the present, the millivolt signal is shown simply as transmitted to a potential recorder. The telemetering of an amplified signal to actuate a solenoid-operated valve will be investigated at a later stage (although no difficulties are anticipated), following the successful laboratory demonstration of a stable and significant potential response by the electrode system. In such a prototype installation it may become necessary to make provision for some (sewer) upstream flow to wet the electrode system in advance of the initial slug of combined or storm sewage following a period of prolonged drought. Aerosol spray application after a period of dryness to rejuvenate the electrodes or buoy suspension of the system are other alternatives to maintain the cell system in good operating condition. Details to provide such an advance flow have been omitted from the present diagram pending further investigations, not included as part of the first year phase of these investigations.

A photograph of the complete laboratory demonstration system is shown in Figure 5.

B. Synthetic Sewage Experimentation

Synthetic sewage substrate was prepared in accordance with the composition developed by Weinberger and Sawyer (17). The exact composition is shown in Table iv.

TABLE IV

Composition of Synthetic Sewage

(per liter of North Andover tap water)

Chemical	Amount
Nutrient Broth	100 mg
Urea	30 mg
Castile Soap	50 mg
Soluble Starch	100 mg
Diatomaceous Earth	25 mg
Sodium Chloride	30 mg
Potassium Chloride	7 mg
Calcium Chloride	7 mg
Magnesium Sulfate	5 mg
Aluminum Sulfate (18 H_2O)	5 mg
Disodium Hydrogen Phosphate	25 mg
Sodium Bicarbonate	168 mg

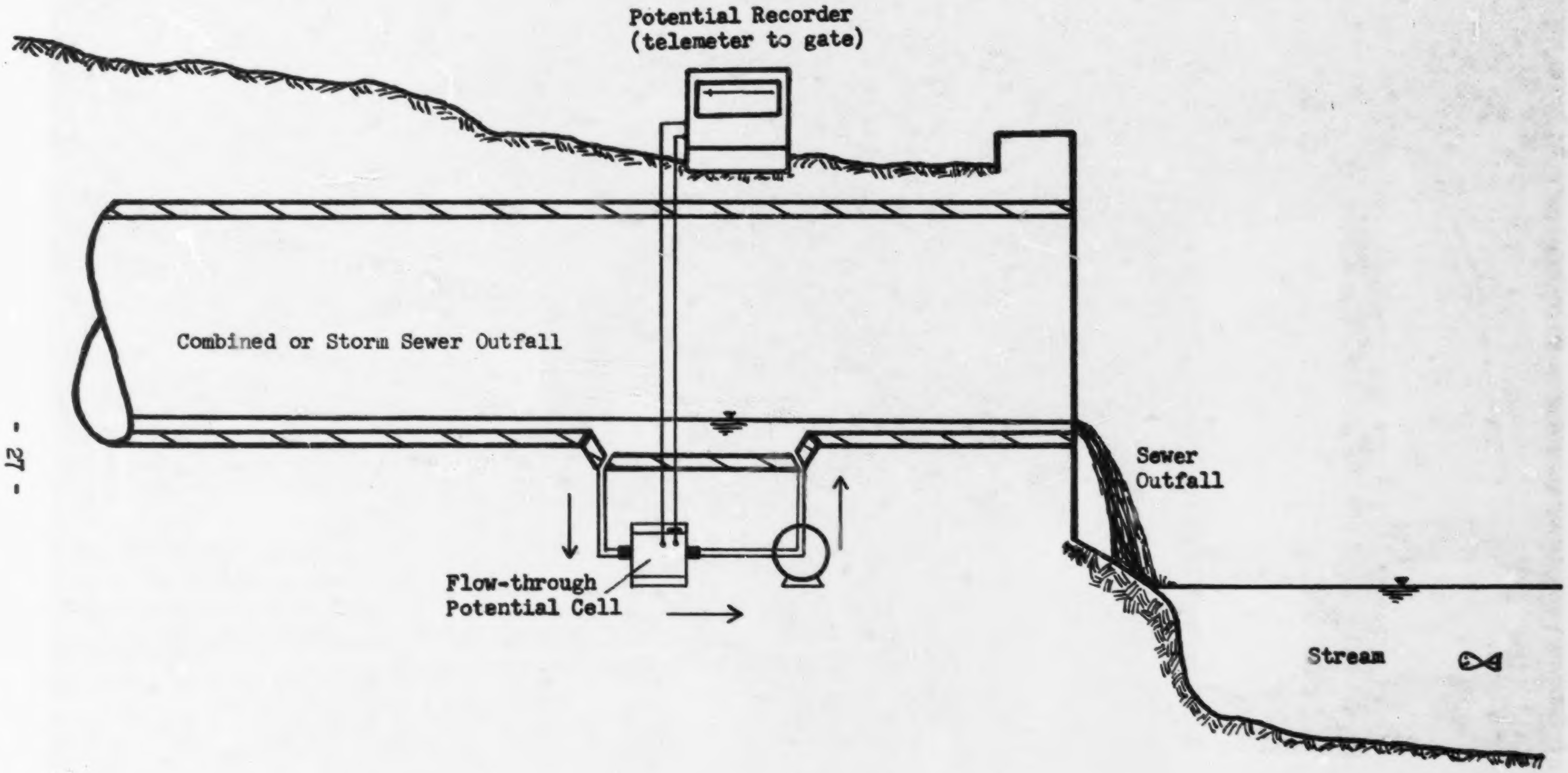

Potential Recorder
(telemeter to gate)
Combined or Storm Sewer Outfall
Sewer
Outfall
Flow-through
Potential Cell
Stream

Figure 4 Conceptual Design of Electrode Potential Control Installation

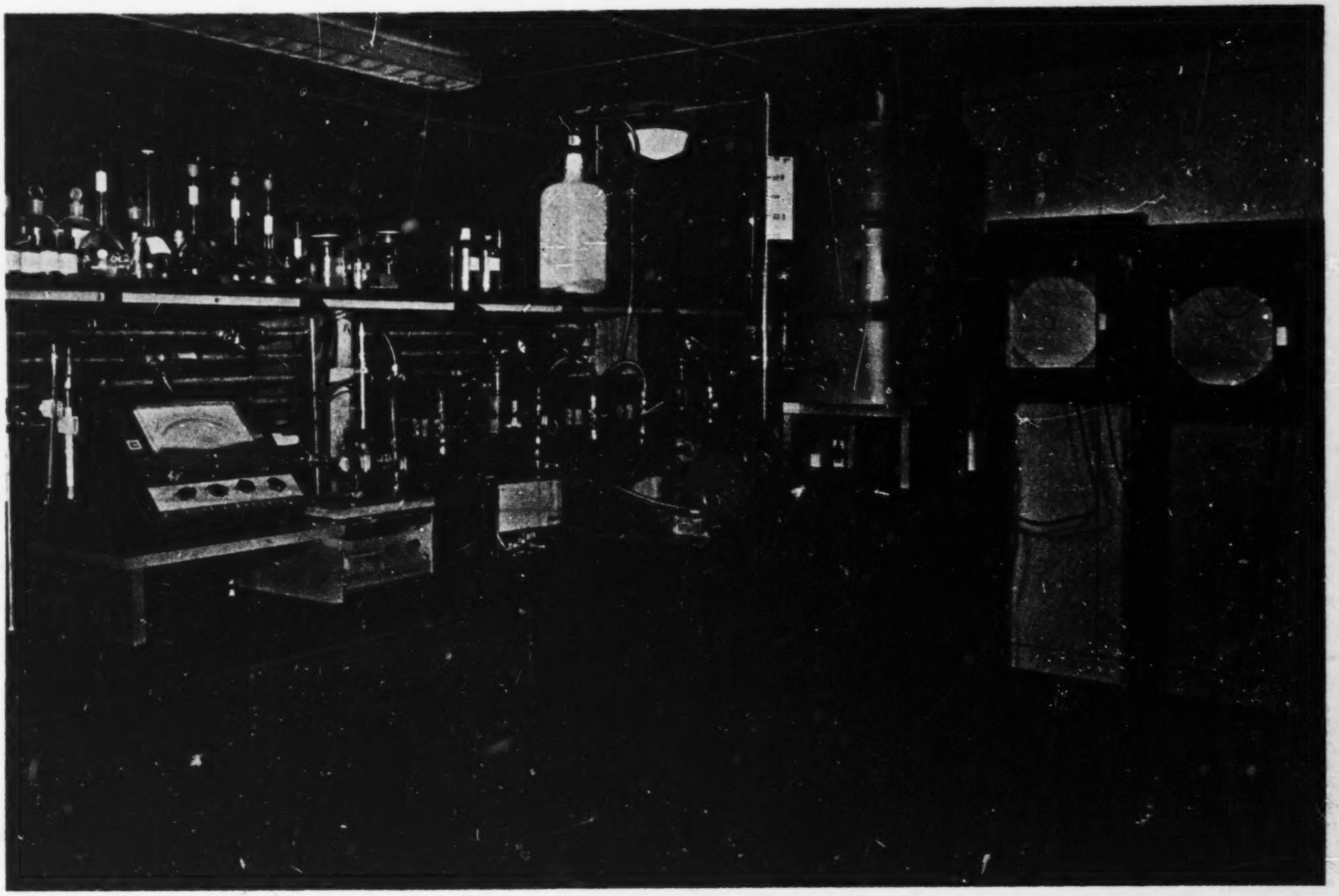


Figure 5. Laboratory Demonstration System

Considerable delay was experienced in obtaining the Nutrient Broth from the supplier and therefore it was prepared by mixing its two separate components on the basis of 3 gms Bacto-Beef Extract with 5 gms Bacto-Peptone (18). A total of three (3) liters of synthetic sewage was prepared for the initial BOD run to determine its actual strength. Sufficient stock solutions were prepared for 30 gallons of synthetic sewage in accordance with the procedure outlined by Weinberger and Sawyer (17).

Domestic sewage from Lawrence, Massachusetts, for seeding, was obtained from the Lawrence Experiment Station, Massachusetts Department of Public Health, on July 7, 1969. Following its use for seeding of the initial synthetic BOD run, the remainder of the seed was frozen for replication in future runs.

The initial BOD run was set up with a 25% dilution of unseeded synthetic sewage and 0.5%, 1%, 2% and 4% dilutions of seeded synthetic sewage. The latter four dilutions were seeded with 0.5 ml and 1.0 ml of diluted (half-strength) settled Lawrence sewage, respectively.

The first BOD run was designed to obttain initial (15 minute), three-day, five-day, seven-day, ten-day and thirty-day readings. All BOD samples were run in triplicate. Summaries of the DO and BOD data were presented in Monthly Progress Letter No. 4 (19).

The data showed that the 25% dilution of synthetic sewage (unseeded) ran out of DO in less than three days. This pointed to the possibility of contaminated chemicals and dilution water.

The seeded synthetic sewages (0.5%, 1%, 2% and 4% dilutions), seeded with 0.5 ml and 1.0 ml of half strength Lawrence sewage, respectively, exhibited a higher BOD for those samples to which less seed had been added. The seed (settled Lawrence sewage) may have contained toxic or inhibitory chemicals.

These vagaries in the dissolved oxygen data and difficulties with the BOD data led to checking the procedure carefully.

The cause of the spurious data was traced ultimately to the use of a wrong alkaline KI solution and contaminated compressed air, used for the dilution water.

In the meantime, examination of electrode potential response with real sewage was initiated rather than a continuation with the synthetic medium. This departure from the work schedule was mutually agreed upon with the concurrence of the Project Officer in order to not fall behind in the fact-finding phase of these investigations.

C. Conditions Imposed for Proper Potential Measurement

1. Different Types of Electrode Systems and Response

All electrode systems consist of two electrodes: an inert, noble metal electrode and a reference electrode half cell.

Examination of the response of different types of cell systems (Pt-Cal, Ag-Cal, Pt-Cu) was undertaken and different types of electrode designs (immersion and flow-through) calibrated and results compared against standard potentials from the leterature for such well-defined redox systems as: quinone-hydroquinone: Fe(II), Fe(III); $SO_3{=}$, $SO_4{=}$; Ce(III), Ce(IV); and the ferricyanide, ferrocyanide system.

Work to develope a non-fouling reference electrode (Cu or Ag plate) together with a thin-film Pt-encapsulated electrode has been underway[a] It was hoped that this system, with the non-fouling reference electrode continuously immersed and the noble Pt readout electrode alternately wet and dry (if necessary aerosol sprayed or buoy suspended), would ultimately produce the permanent potential measuring system; provided the reference electrode can withstand the bacterial action from growths. The purpose of the Cu electrode is to provide a more rugged reference electrode, capable of withstanding the aggressive action of storm and combined sewage and produce a more dependable, stable electrode potential in prototype installations. This electrode system was investigated in parallel with the other systems.

In addition to the regular immersion type of electrode systems, the 3/8-in. diameter Ag, AgCl-Pt flow-through cells[b] have given the most stable, reproducible and accurate readings.

Initially, standardization of these electrode systems was by means of the quinhydrone system. The variation of its potential with pH is shown in Table V.

TABLE V

Variation of Electrode Potential of Quinone-hydroquinone System

$$2H^+ + C_6H_4O_2 = 2e^- + C_6H_4(OH)_2$$

pH	Readout, mv
1	640.7
4	463.4
7	285.1
10	108.8

The equation for a saturated solution of quinhydrone at 25°C is:

$$E_o = 0.6998 - 0.0591\ pH \qquad (2)$$

---

[a] Manufactured by Delta Scientific Corp., 120 East Hoffman Avenue, Lindenhurst, New York 11757.

[b] Manufactured by Fischer & Porter Company, Warminster, Pennsylvania 18974.

Other potential systems which have been employed include: Fe(II), Fe(III); SO_3=, SO_4=; Ce(III), Ce(IV); and ferricyanide, ferrocyanide. Some results obtained during the calibration experiments with the Ce(III), Ce(IV) system are shown in Table VI. This data shows good agreement between the Pt-Cal and the thin-film Pt-encapsulated and non-fouling Cu reference electrode systems(c).

TABLE VI

Response of Electrode Systems (a)

(Std. Potential Ce(III), Ce(IV) = 1217.2 mv at 25°C.)

10 mg of Ce(IV) mg of Ce(III)	Pt-Cal Electrodes (b) (mv)	Pt-Cu Electrodes (c) (mv)
0	1212	1227
	1211	1228
1.0	1210	1227
	1208	1226
2.0	1204	1224
	1202	1222
3.0	1200	1221
	1198	1220
4.0	1195	1219
	1192	1218
5.0	1191	1217
	1190	1215
6.0	1189	1213
	1188	1212
7.0	1187	1211
	1184	1210
8.0	1182	1210
	1181	1209
9.0	1180	1208
	1180	1207
10.0	1179	1206
	1178	
11.0	1177	1204
	1176	
12.0	1175	1202
	1172	
13.0	1172	1201
	1171	
14.0	1170	1200
24.0	1160	1190

(a) Duplicate readings at one minute intervals
(b) Manufactured by the Leeds and Northrup Company
(c) Manufactured by the Delta Scientific Corporation

Experiences with the Fe(II), Fe(III) system have been less than satisfactory, the best value acheived was E_h = 476 mv as compared to a standard potential value of 525.4 mv at 25°C from the literature. The sulfite-sulfate system produced no stable value, the potential kept drifting at a steady rate. Much greater success in determining electrode response was achieved with the Ce(III), Ce(IV) system, as shown by the values reported in Table VI. After a number of known redox systems were evaluated (including quinhydrone), a ferricyanide, ferrocyanide system [K_3 Fe $(CN)_6$ solution] was chosen ultimately as the standard potential because of its very stable potential over a long period of time. Data showing this stability were presented in Progress Letter Number 5.(20).

The flow-through cell uses the silver-silver chloride half cell which is similar in construction to the calomel half cell. It consists of a silver electrode, immersed in a saturated KCl reservoir connected to the sample by a salt bridge consisting of saturated KCI solution diffusing through a porous porcelain tube (21). The Ag-AgCl cell has a half cell potential of +197 mv at 25°C (as compared to 220 mv for the standard calomel). This type of half cell, together with either a gold or a platinum electrode, was used successfully as the flow-through(a) potential cell in these investigations.

More recently, while investigating polarization resistance techniques, another flow-through potential sensor cell, claimed to have a high degree of accuracy, was developed. This system (b) appears to have an improved liquid junction and self-pressurization for the Ag, AgCl reference cell. An extremely short transmission cable should result in essentially no transmission leakage from the platinum electrode. Another advantage claimed is the extremely high impedance of the amplifier which senses the output of the Pt electrode. One of the disadvantages appears to be the need of an amplifier which increases the cost of this system appreciably.

2. Types of Monitoring Systems

There are two basic designs of potential cell systems that are of interest: 1) the stationary cell and 2) the flow-through cell. Either of these cell designs may employ various types of electrode pairs; one a standard half cell, the other an inert, noble metal electrode (platinum, gold, etc.).

When the electrodes of a stationary cell system are immersed the solution must be agitated continuously to prevent polarization of the noble metal electrode. This electrode must also be cleaned periodically to assure correct response.

(a) Manufactured by Fischer & Porter Company.

(b) Manufactured by Universal Interloc, Inc., 17401 Armstrong Avenue, Santa Ana, California 92705.

The flow-through cell consists of a platinum electrode and a standard silver, silver chloride electrode which is in intimate contact with a saturated KCl solution, kept under a guage pressure so that it will diffuse through the porous membrane and make contact with the liquid in the flow-through cell. This cell, unlike the stationary cell, presents no obstruction to the flow as may be seen in Figure 6, and therefore is not easily plugged by fibrous material or grease present in wastewaters.

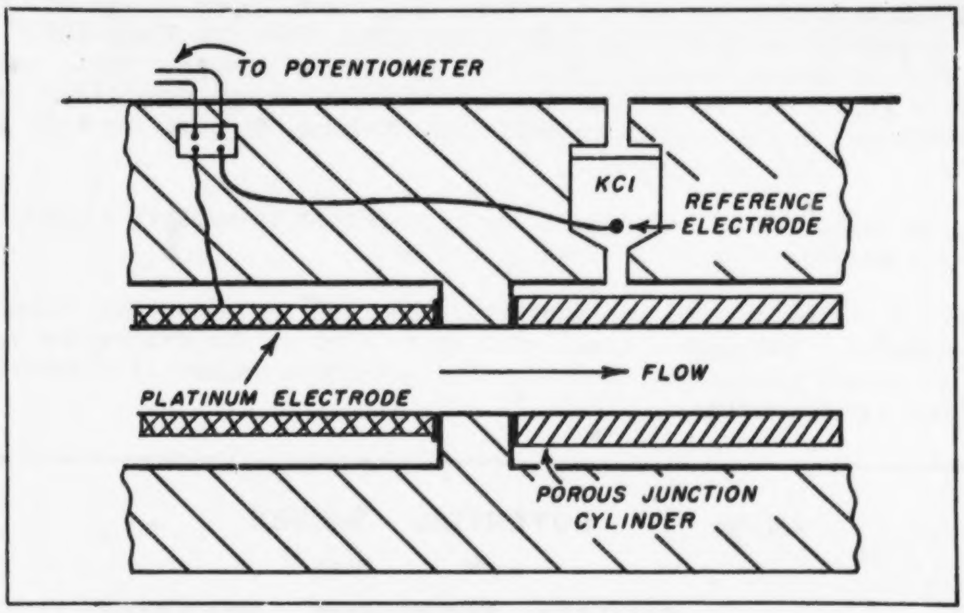


Fig. 6 —Cross section of a flow-type cell for measuring oxidation-reduction-potential

Polarization of the noble electrode in the flow-through cell has been avoided by a large paltinum electrode and a rapid flow rate. Earlier work showed that a flow-through velocity of at least 1 ft/sec prevents polarization amost indefinitely (22). The entire electrode assembly is housed in a Teflon block along with the KCl reservoir.

Any good potentiometer may be used in conjunction with these cells to measure the potential difference. In the present experiments three meters of this type, a Leeds and Northrup pH and mv meter, a RCA V.T.V.M. and a Fischer and Porter recording mv meter were used interchangeably.

3. Range of Potentials

As sewage flows through its delivery system, it is treating itself as it travels. Fresh sewage from a household may exhibit high positive potentials due to the presence of dissolved oxygen. When introduced into the delivery system, it is assimilated into a body of water where the conditions are not always conducive to the retention of an aerobic state. Because of high oxygen uptake at the water surface, any reaeration is likely to be cancelled out, leaving only the sewer stream oxygen to be depleted before anaerobiosis may set in.

While fresh sewage will exhibit high positive potentials (especially in the present of DO), when introduced into sewerage systems not conducive to the retention of an aerobic state, the potential will fall significantly.

Thus, while potential drops are small (generally exhibiting positive or small negative values) when DO levels are above 1 mg/l, sharp drops (highly negative values) are observed when DO concentrations fall below 1 mg/l. (Note: Compare values in Table VIII). Okey, et al. (23), found a relatively small decrease of potential below 5 mg/l DO until the DO fell to below 1.0 mg/l when the rate of potential drop increased sharply with a drop of 425 mv (from +75 mv to -350 mv) as the dissolved oxygen concentration fell from 1.0 mg/l to approximately 0.1 mg/l. Since anaerobic conditions are more likely to become established when velocities are low and detention periods in sewers long, these types of systems are likely to exhibit low electrode potentials which does not limit the feasibility of using electrode potential systems in sewage. Thus, the ultimate objective, to prevent the discharge of sewage exhibiting these characteristics by continuous potential monitoring, appears feasible to achieve.

Collection systems which are small may be expected to exhibit higher potentials because of shorter detention time.

In Figure 7, Dirasian (24) has indicated the range of potentials likely to be encountered. Although a range of 0 mv to +400 mv for wastewater is shown, it is not ususual to find negative potential values if anaerobic conditions are impending.

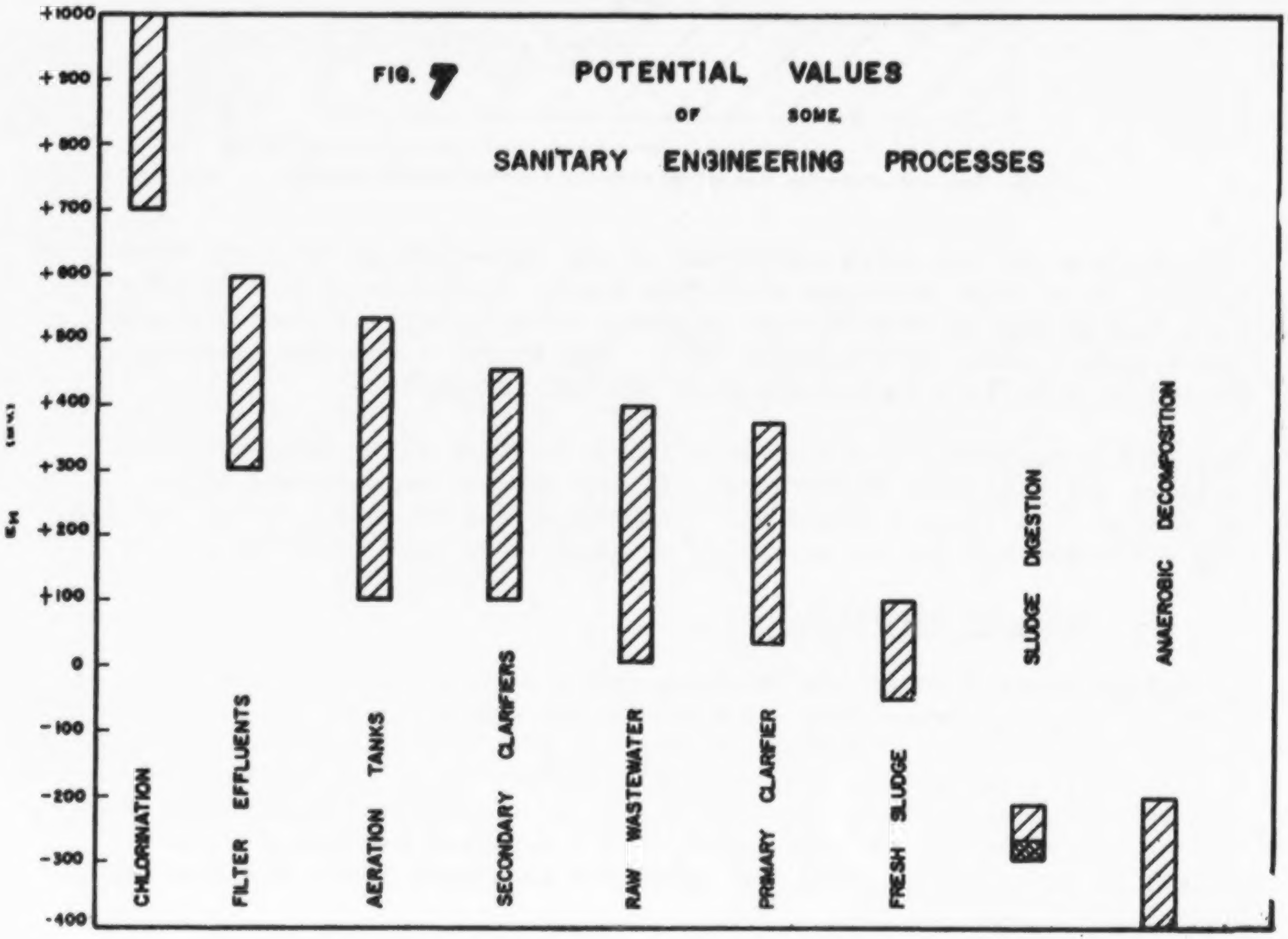


FIG. 7 POTENTIAL VALUES OF SOME SANITARY ENGINEERING PROCESSES

4. Sensitivity of Potential to Sewage Strength

As reported in the literature, the response time of a potential system varies, depending on the substrate material. The time interval to obtain fairly steady potentials was found by Henry (25) to vary from 2 to 5 to 10 minutes in sewage. According to Hood (26) the time interval in sewage is 10 to 30 minutes. However, both authors used immersion electrodes in their work rather than a flow-through type cell.

Another advantage of the flow-through cell is its greatly improved response time. The response time of the Fischer and Porter flow-through cell to the standard ferricyanide, ferrocyanide potential system was found to be less than one second (19).

5. Effect of Interfering Substances

A major problem that develops when using stationary electrodes to measure potentials of flowing systems is the accumulation of polarizing substances on the electrodes. Since stationary electrodes are obstructions in the flow path, it is likely that non-polar substances such as oils, grease and sewer slimes deposit themselves on, or coat the electrodes. Figure 8 shows the effect of electrode polarization on a stationary system after it had been immersed in sewage for approximately ten (10) days without cleaning. The potential record of the same system for the entire previous week (starting August 19, 1969 is shown in Figure 9. A record of the sewage substrate temperature is shown in Figure 10, indicating that temperature control within 25 ± 0.5°C, or better, was achieved during the controlled laboratory investigations.

The flow-through cell was also developed to overcome the problem of polarization, utilizing the inside surface of a pipe as the noble metal electrode. It presents no longer a flow path obstruction and deposition of material on the electrode is minimized or eliminated. The potential record, using a flow-through cell, for the week beginning August 29, 1969, is shown in Figure 11. Beginning with a potential of approximately -210 mv, the potential gradually rose to -120 mv in about 4 days. When the peristaltic pump was turned on (10:45 a.m. on September 2, 1969) the potential dropped to -250 mv due to the anaerobic substrate being delivered to the cell from the bottom of the 30-gal tank. The stepwise pattern on the chart is due to electrical interference from the large heating unit of the thermostated Warburg respirometer.

A record of the mv signal from the flow-through cell without the temperature bath (holding room and sewage temperature constant at 20°C) is shown in Figure 12. This seven-day chart, started on September 3, 1969, shows a fairly steady potential of about -200 mv for two days, which then gradually decreased to -240 mv at the end of the week. This record of the potential is considerably smoother and demonstrates that continuous potential recording can be achieved successfully.

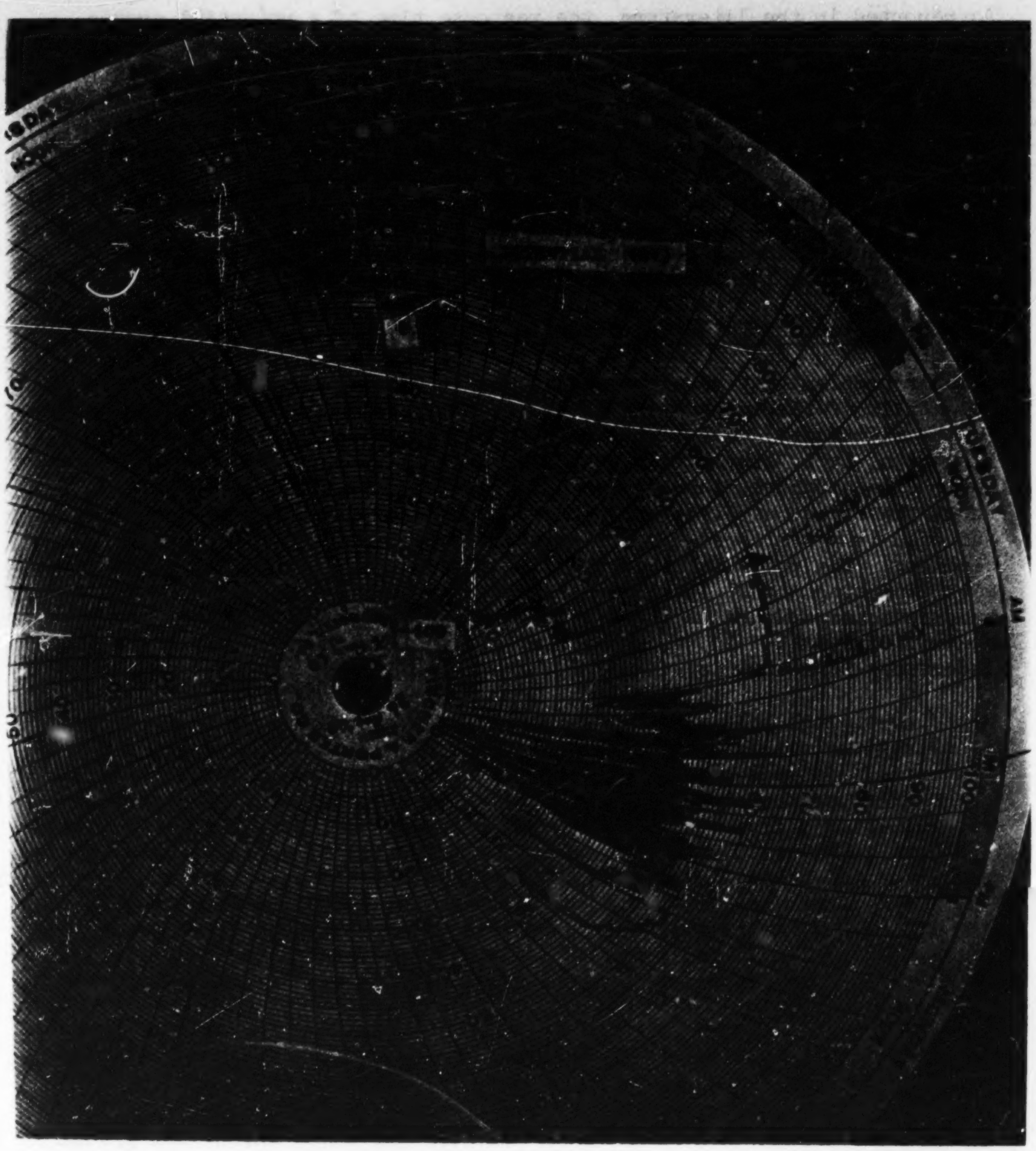


Figure 8, Polarization of Immersion Electrodes

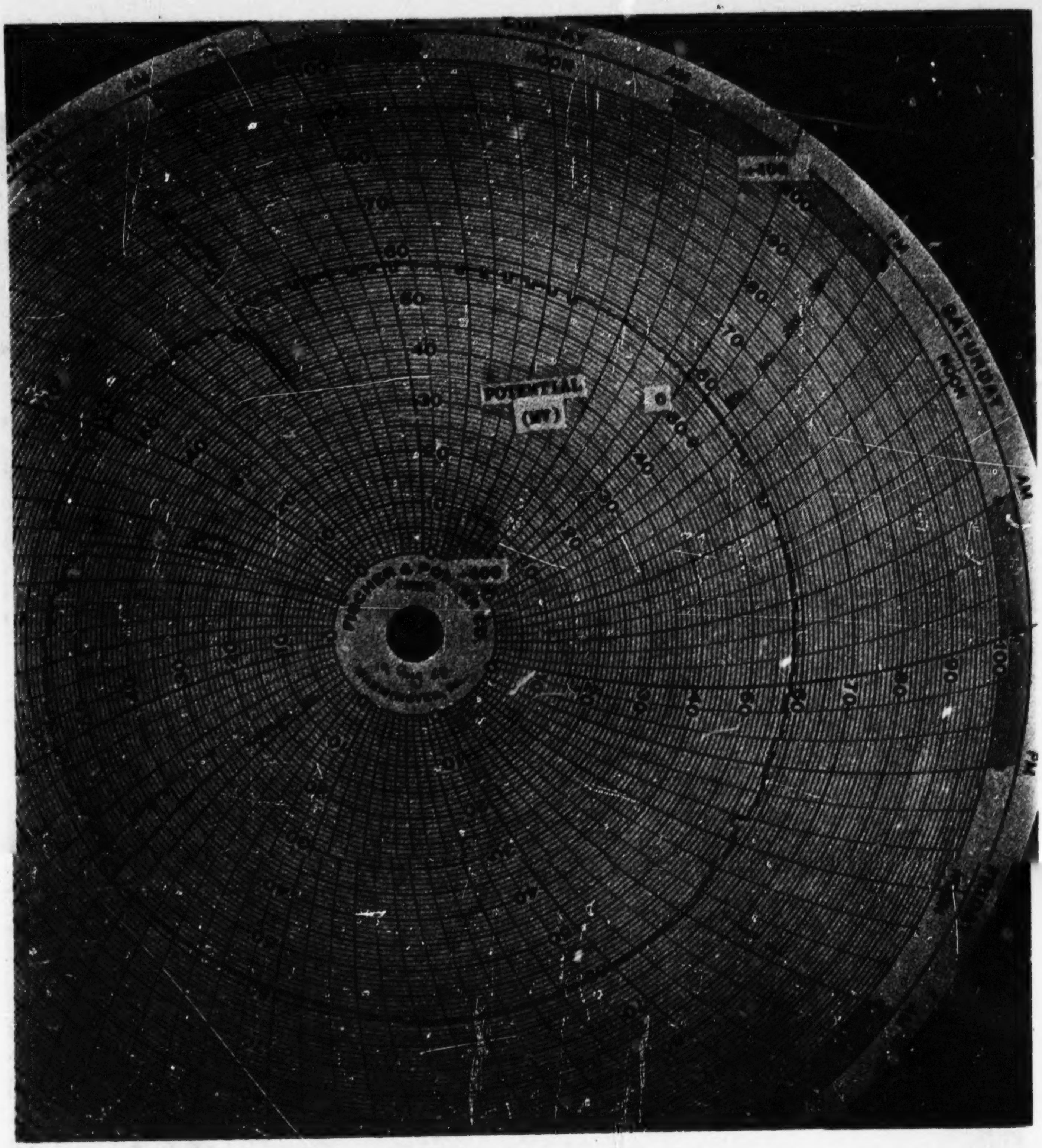


Figure 9. Potential of Clean Immersion Electrodes

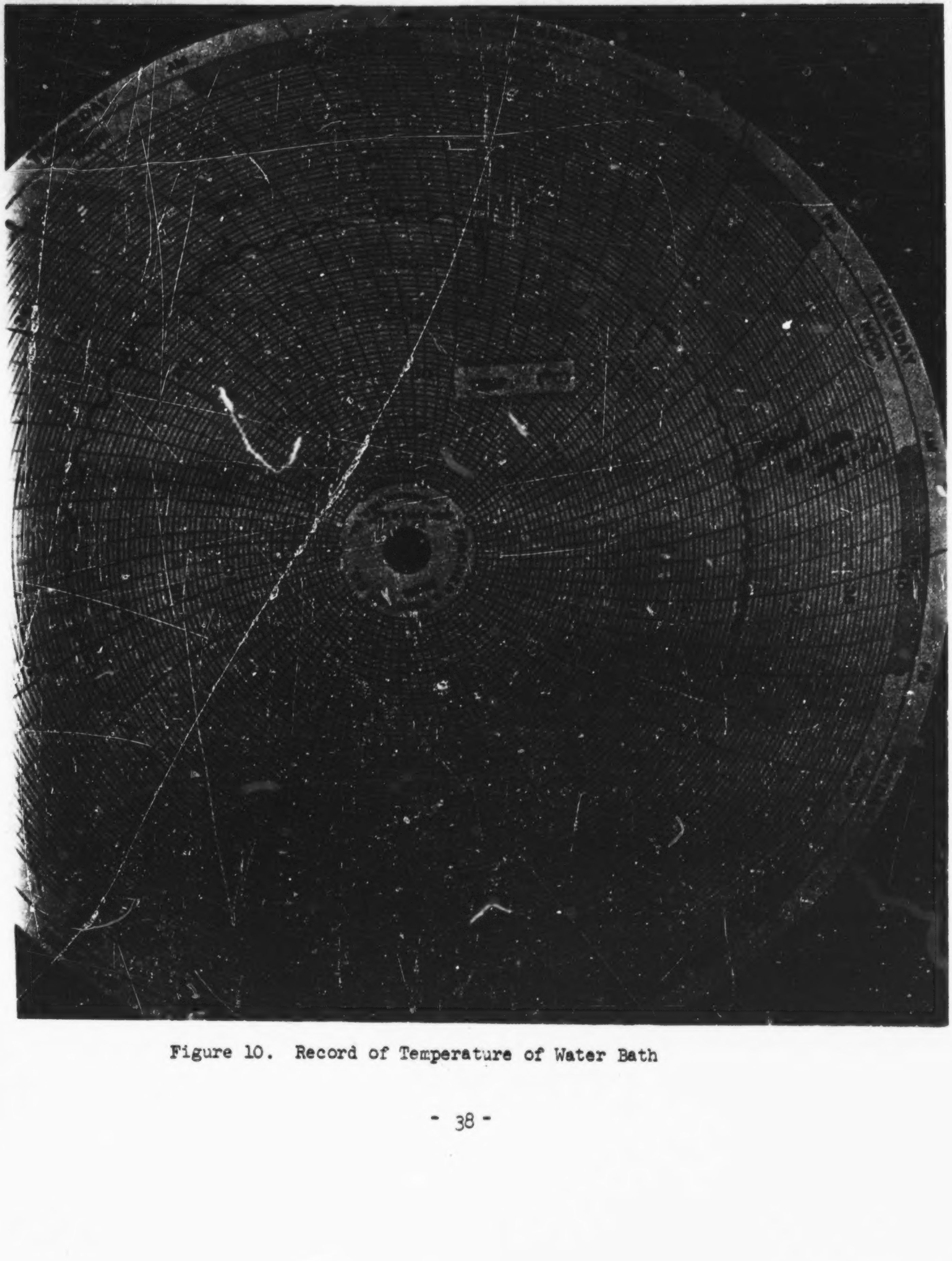


Figure 10. Record of Temperature of Water Bath

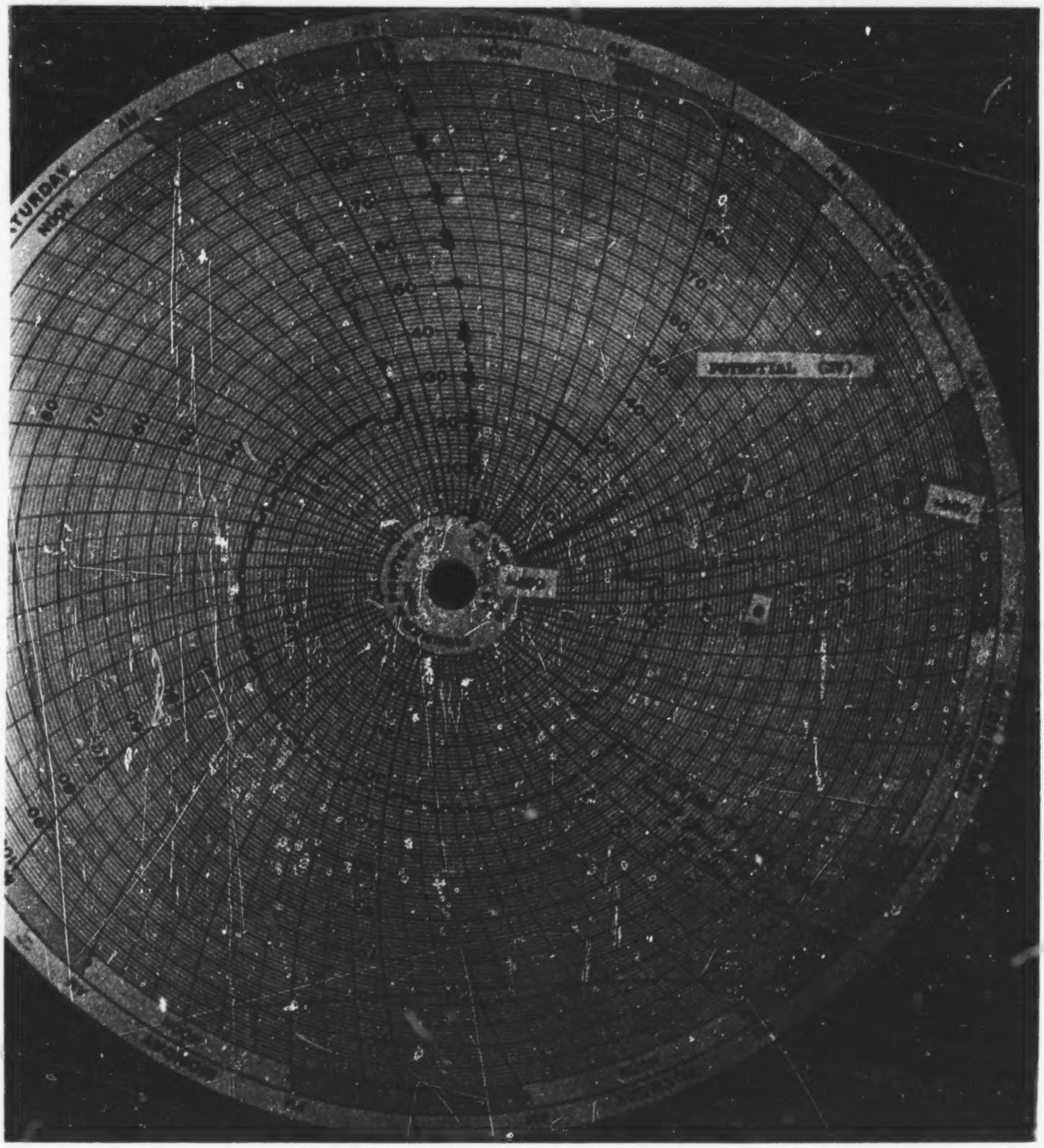


Figure 11. Potential Record of Flow-Through Cell
(With electrical interference)

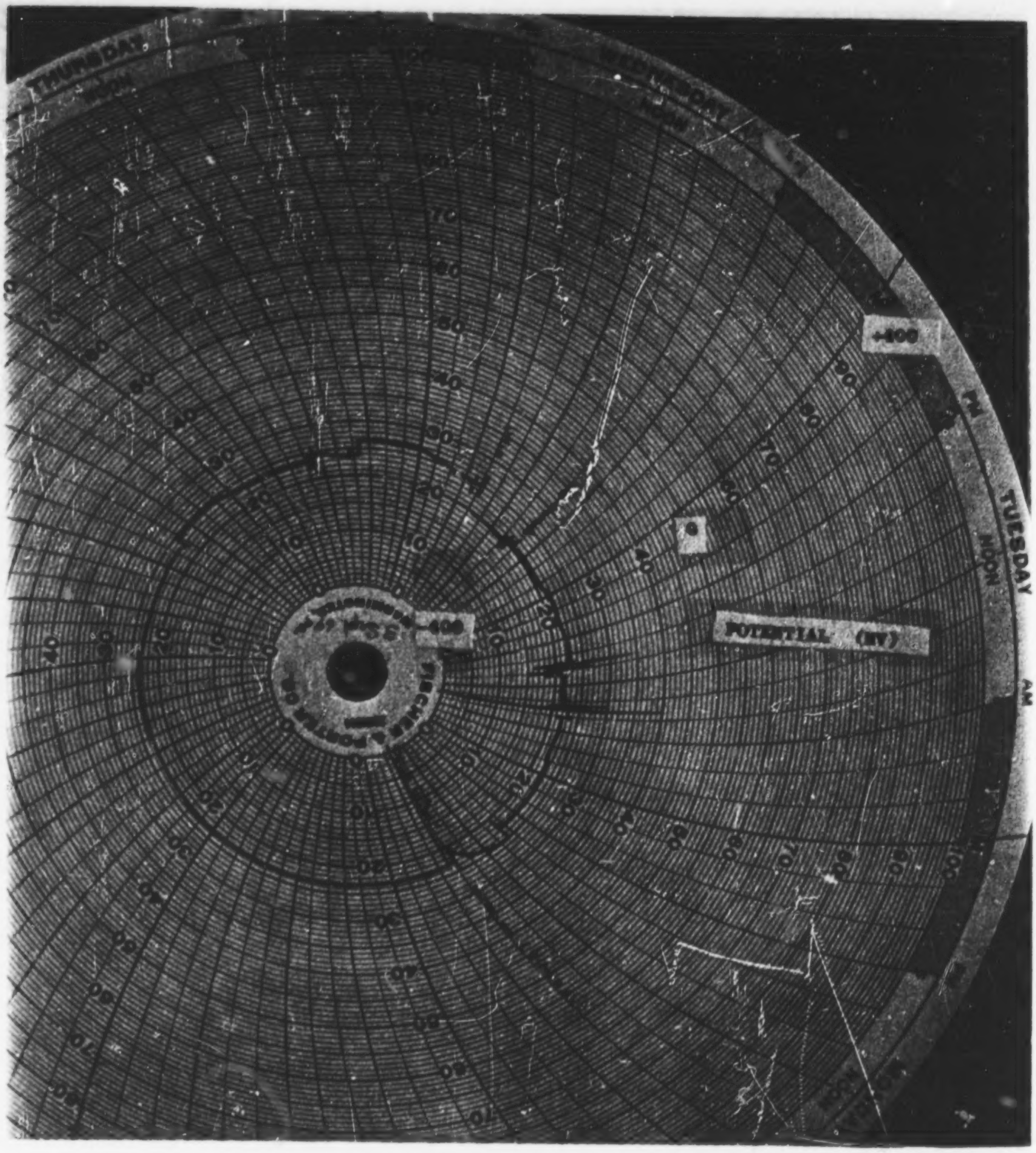


Figure 12. Potental Record of Flow-Through Cell
(without interference from electrical heater)

6. Maintenance of Flow-Through Cell

A perfectly clean noble metal electrode is essential for proper potential measurements (25). Various methods for the care and cleaning of stationary electrodes have been recommended and are practiced.

The cleaning of the flow-through cell assembly is accomplished easily with a test-tube brush and plenty of water (21). In extraordinary cases, after prolonged operation of the cell, it may be necessary to use a dilute solution (1.5%) of HCl to rejuvenate the noble metal electrode.

7. Characterization of Different Types of Drainage

a) Variables Encountered in Sewage

The chemical and physical components of sewage are many and varied. An exact characterization of sewage is difficult and probably futile. Nevertheless, a number of investigators have tabulated concentrations of certain parameters to characterize a weak, medium or strong sewage, varying for example in BOD strength from 100 to 200 to 400 ppm, respectively.

Other variables are also of increasing interest, such as phosphorus, nitrogen and sulfur compounds. Weibel (27) estimated concentrations of nutrients in a "medium" strength sewage as follows:

Total N (as N) = 40 mg/l
Total PO_4 (as PO_4) = 10 mg/l

Estimating the concentrations of nutrients to be found in sewage, Sawyer (28) reported similar values:

NH_3 - N = 20.0 mg/l
NO_3 - N = 0.0 mg/l
Organic N = 15.0 mg/l
PO_4 - P = 8.0 mg/l
Organic P = 2.0 mg/l

The accumulation of sulfides in sewage is a function mainly of the sewerage system. Such factors as detention time in sewers, flow velocity, sewer slime composition and other variables have been studied intensively by a number of other investigators (29)(30)(31)(32)(33)(34) and estimation of concentrations appears to be very difficult. More will be stated later about the presence of sulfides and their effect on the potential.

b) Urban Runoff

Drainage from urban areas is not as clean as it was once thought to be. The concentration of solids and nutrients, as well as BOD loadings and other variables encountered in several studies (1)(3)(12)(35)(36) have indicated that urban runoff should receive increased attention to help alleviate pollution. Studies of selected areas in Cincinnati; Chicago; Ann Arbor, Michigan; Stockholm, Sweden; and Pretoria, Union of South Africa have shown BOD values as high as 185 ppm (Chicago) with a mean value of about 30 ppm and coliform as high as 240,000 MPN/100 ml (1). Total phosphorus concentration as high as 4.4 ppm was reported recently in the drainage for a street in Chicago (12). The range of solids concentrations reported shows that this parameter is entirely dependent upon the topography, hydrologic and geologic characteristics of the drainage area under consideration. However, these characteristics must be evaluated in reference to the pollutional load carried by the early flushing of the sewerage system into the nearest watercourse.

c) Agricultural Drainage

The superimposed loads of nutrients from the increased availability and utilization of commercial fertilizers are of a much greater magnitude than was generally recognized. More intensive land use and farming practices throughout the world are contributing to increased pollution of streams, lakes and oceans. The concentration of total phosphorus in Lake Constance on the German/Swiss border has increased at an alarming rate. In 1945 the total P concentration was 0.5 mg/l, by 1955 this concentration had risen to 5 mg/l and in 1967 reached a level of 10 mg/l; much of this rapid increase being ascribed to more intensive farming techniques. At the same time, several large cities have been vying for the water resources of Lake Constance as their future water supply.

Sylvester (37) has reported values indicative of the nutrient content of agricultural drainage which show total phosphorus concentrations of the order of 0.4 ppm and total nitrogen as high as 3 and 4 ppm. Irrigation uses involve enormous quantities of water (as measured by acre-feet; 1 acre-foot = 326,000 gals.). While these concentrations may still appear small, they represent many tons of nutrients unloaded and being discharged into this Nation's waterways.

8. Effect of Sulfides on Electrode Potential

For a better understanding of the effect sulfides on the electrode potential, some relationships between bacterial growth, sulfides and electrode potential may be helpful.

The generation of sulfides in sewage takes place as the result of two biochemical processes: 1) decomposition of S-containing organic compounds by facultative bacteria, and 2) reduction of sulfates by the bacteria Sporovibrio desulfuricans. Each requires its special environment to function properly and sewage and sewer systems provide a viable surrounding for both. The facultative bacteria populate the stream of the sewer and produce sulfides as a result of their metabolic processes in which complex organics in the stream are broken down into more simple forms. The generation of sulfides in this manner is generally small, except where unusually long mains or long ocean outfalls are used. In such cases, as in slow moving gravity flow systems, anaerobic conditions exist in the flowing sewage and sulfide generation may reach considerable proportions. The second process involves reduction of sulfates by S. desulfuricans. This strain of obligate anaerobes is found in the waste stream, although generally in relatively small concentrations (average = 258 orgs/ml according to Eliassen, et al (33). The presence of these sulfate-splitting bacteria in sewer slimes, however, reaches higher populations (6,000/ml) and the most active sulfide generation takes place in the slimes. The stream acts as a source of sulfates for these sulfur ingesting bacteria.

It is possible to visualize a free-flowing sewer as being composed of two zones of potential. The surface and upper body of the flow may exhibit a positive E_h in the presence of oxygen diffusing into this flow. However, in the lower levels oxygen has already been consumed by the biochemical reactions. The sewage and slime interface, as well as the slime growths, exhibit low potentials as indicated by the presence of S. desulfuricans. These organisms exist in large quantities only in potential ranges of -200 mv to -300 mv, indicating anaerobic conditions generally accompanied by the active generation of sulfides.

There are two ways in which sulfides and sulfide-producing bacteria may affect the potential: 1) by generation of sulfides in the stream and from slimes to become factors in the redox level, and 2) by scouring of the slimes within the sewer, such as during periods of intense rainfall.

From separate studies (30)(38) conducted on force mains in Miami and Los Angeles, it has been established that sulfide accumulation depresses the potential level significantly. At Miami, in a four-mile force main leading to the treatment plant, the potential dropped on the average from -236 mv to -308 mv ($E_{cal.}$), while total sulfides increased from 0.8 mg/l to 7.0 mg/l. Bargman, et al (30) reported that in the nine-mile stretch of force main leading to the Hyperion Treatment Plant in Los Angeles potential levels dropped from +248 mv to +48 mv, with an increase of total sulfides from 0.2 to 1.8 ppm. All other characteristics reported remained constant. Sulfide production may be expected to be more active in sluggish sewer systems. If environmental conditions are conducive to the growth of sulfate reducing slimes, they will contribute directly to the depression of the potential.

In both cities, the sewage streams were devoid of dissolved oxygen. There is a possible correlation between the potential drop and depletion of DO; after that with sulfide concentration in the anaerobic range. The mechanism of sulfide production requires that dissolved oxygen be depleted before facultative bacteria begin breaking down complex organics in the stream to form sulfides. Once anaerobic conditions have become established, the sulfides formed by the facultative bacteria will depress the potential level. When sufficiently low levels are reached, serious sulfide production is started by anaerobic bacteria.

The effects from scouring of sewer slimes from the interior walls of sewers presents another major pollutional control problem and one that lends itself to modulation by potential-controlled flow. The degree of mixing and the characteristics of the slimes will affect the potential of the sewer discharge. The hydraulic characteristics of the sewerage system and the intensity of rainfall will have a great effect upon the rate at which slimes are scoured and the total amount of scouring which will take place.

As part of the current laboratory demonstration studies, sulfides were analyzed along with determinations of the potential whenever practicable. These values are shown in chronological order in Table VII. It is apparent that beginning with the observations of October 24(#), as the sulfide concentration increased the potential became increasingly negative. The sulfide concentration was increased by the addition of $Na_2S \cdot 9H_2O$ during the last four observations as shown in Table VII, Part A.

To check on the performance of the electrode system and to confirm the reproducibility of results, the same sewage substrate (30-gals sample) used previously during the sulfide addition was aerated and the changes in potential, total sulfide concentration, dissolved oxygen and BOD noted. The results are shown in Table VII, Part B. These results show fairly good agreement with those obtained while the substrate became increasingly anaerobic.

Further experimentation to check the sensitivity and reproducibility of the electrode potential was conducted with another 30-gallon samble of sewage. However, in this experiment the sulfide concentration was not artificially increased. The results are presented in Table VII, Part C. Again, fairly good agreement between the potential and sulfide concentrations with the values obtained in the previous parts of this experiment, was observed.

Although perhaps of questionable value, an effort was made to relate the dissolved oxygen concentration with the electrode potential in the presence of sulfides. Okey, et al (23) has reported a drop of potential from +75 mv to -350 mv as the dissolved oxygen concentration fell from 1.0 mg/l to about 0.1 mg/l. For the data presented in Table VII, Part A, dissolved oxygen concentrations were zero during the period of 9/8 thorugh 10/24(*). A small amount of DO (perhaps 0.1 to 0.5 ppm) was available in the substrate on 10/26, the day on which the minimum negative potential was observed (-150 mv).

It is extremely difficult to separate the effect of dissolved oxygen and sulfides on the electrode potential. However, by rearranging the appropriate data from Table VII some general facts seem to stand out:

(*) See Table VIII for complete DO data. The DO values were analyzed and found to be zero for 9/8, 9/10, 9/11, 9/23, 9/29 and 10/24.

(#) This sewage sample was collected from the Lawrence Experiment Station, Lawrence, Massachusetts on October 22, 1969.

TABLE VII

Effect of Total Sulfide Concentration on Potential

Part A:

Date	Total $S^=$ Concentration in Sewage	Potential Reading(b)
(1969)	(mg/l Total Sulfide as S)	(mv)
8/29	3.00	-220
9/3	4.80	-228
9/8	5.41	-236
9/10	6.12	-240
9/11	0.51	-248
9/23	3.28	-232
9/29	0.10	-210
10/24	5.60	-300
10/26	4.35	-150
11/3	7.55	-258
11/3	8.10(a)	-306
11/3	10.40(a)	-357
11/3	20.10(a)	-454
11/3	30.10(a)	-511

Note: (a) due to Na_2S addition
(b) Fischer & Porter Cell at 20°C

Part B:

Time interval of Aeration (hr)	Potential(b) (mv)	Total Sulfide(c) (mg/l)	D.O.(c) (mg/l)	B.O.D.(c) (mg/l)
0	-511	30.1	0.0	--
0.5	-250	4.03	0.0	220
1	-100	0.54	2.3	50
2	+95	0.0	5.1	0.0

(c) Average values of duplicate samples.

Part C:

Time interval of aeration (hr)	Potential (mv)	Total Sulfide(c) (mg/l)	D.O.(c) (mg/l)	B.O.D.(c) (mg/l)
0	-320	6.59	0.0	275
0.5	-168	3.12	1.8	108
1	+43	0.0	5.7	43
2	+157	0.0	6.9	0.0

(c) Average values of duplicate samples.

Electrode Potential (mv)	Dissolved Oxygen	$S^=$ Concentration
-150	0.1 to 0.5	4.35
-100	2.3	0.5
+100	5.1	0
+43	5.7	0
-168	1.8	3.12
-236	0	5.4
-240	0	6.1
-248	0	0.5
-232	0	3.2
-210	0	0.1
-300	0	5.6

All other factors being equal, i.e, pH, temperature, etc. of the substrate and environmental conditions (not controlled in these experiments) it appears that: (i) a similar mv range (+100 mv to -210 mv) as that reported by Okey, et al (23) exists when very little or no sulfides are present, (ii) that in the presence of appreciable $S^=$ concentration a potential of -150 mv to -300 mv may be expected, and (iii) the greater the $S^=$ concentration the more negative the potential will be, except when a small amount of DO is present which will exert an attenuating influence.

It appears from these controlled laboratory investigations and previous studies in the field that sulfide production is indicative of a state of low potential and may be the predominant reductant present in extensive sewerage systems with small slopes. Certainly, flows carrying reducing substances of this order will have a detremental impact on the dissolved oxygen reservoir of any receiving waters and must be kept from exerting their damaging influence on bathing beaches, tidal estuaries and other water resources. Controlling the flow from outfalls by the electrode potential should significantly help to minimize such insults to the environment.

9. Poising of Electrode Potential

Although the need for poising the substrate system to obtain reliable potential measurements did not appear necessary throughout the studies reported herein, there was some discussion about the lack of poising of the combined sewage and/or stormwater runoff. Therefore, several limited experiments were conducted to examine the effect of the addition of a phosphate buffer initially to distilled water and then to the sewage substrate.

(a) Experiments with Addition of Sulfide to Phosphate Buffer and Distilled Water

Sulfide ion was added in known amounts to distilled water by itself and phosphate buffer (as specified in the B.O.D. procedure in Standard Methods) and the effect on potential observed, using the standard, immersion-type Leeds and Northrup electrode system at 20°C.

The results are given below:

Sample: 500 ml of Distilled Water

Sulfide Concentration (ppm)	Potential (mv)
0	+300
5	-85
10	-115
15	-120
20	-135
25	-141
50	-182

Sample: 500 ml of Phosphate Buffer

Sulfide Concentration (ppm)	Potential (mv)
0	+300
5	-185
10	-200
15	-210
20	-218
25	-222
50	-235

The buffer appears to have reduced the potential range from 100 to 40 mv.

(b) Experiments with Addition of Sulfide to Sewage with and without Phosphate Buffer Added

A 500 ml sample of sewage was treated with 50 ml of phosphate buffer (as specified in the B.O.D. procedure in Standard Methods) and the sulfide concentration increased by addition of known volumes of $Na_2S \cdot 9H_2O$ solution. The results are summarized below:

Sample: 500 ml of Sewage without added Phosphate buffer

Sulfide Concentration Added (ppm)	Potential (mv)
0	-200
5	-209
10	-213
15	-221
20	-223
25	-230
50	-258

Sample: 500 ml Sewage with 50 ml Phosphate Buffer Added, (initial potential without buffer = -200 mv)

Sulfide Concentration Added (ppm)	Potential (mv)
0	-161
5	-240
10	-240
15	-239
20	-240
25	-240
50	-245

The buffer appears to have reduced the range of potential from 40 to 5 mv.

Based on these limited investigations it appears that the addition of a buffer to sewage may be helpful in stabilizing the potential, although the influence of a strong reductant might be masked. Further laboratory work on this phase is needed.

D. Comparison of Electrode Potentials Against Conventional Sewage Parameters

Laboratory analyses of both standard and non-standard parameters to characterize the sewage and for comparison against potential readings were carried out in accordance with the approved Plan of Operation, beginning on July 24, 1969. Initially only BOD and COD values were determined along with the electrode potentials. As the personnel became more familiar with the laboratory procedures an increasing number of parameters could be determined simultaneously. Instead of the 13 parameters listed in the original Plan of Operation, as shown in Table III, actually a total of 16 parameters were studied ultimately.

A summary of the laboratory analyses against which electrode potentials are compared is shown in Table VIII. Most of these data were obtained in duplicate and triplicate. It may be observed that a total of nine different 30-gals. sewage samples were collected and subjected to analysis between July 23, 1969 and February 9, 1970. The strength of sewage samples as collected varied with five-day BOD values from 109 mg/l to 312 mg/l; total solids ranged from 476 mg/l to 857 mg/l, while the electrode potential ranged from +118 mv to -329 mv. Therefore, sewages varying from weak (or dilute) to strong were investigated. The majority of the samples analyzed exhibited anaerobic conditions as reflected by the electrode potential and corroborated by the sulfide concentrations. Little attempt was made to maintain the sewage in an aerobic state once it had been collected, except continuous gentle stirring. Rather, it was the intention not to alter the sewage substrate and thus it became increasingly septic with time. This procedure broadened the experimental range of the same substrate and permitted investigations of the effect of sulfide concentration on the potential.

From even a cursory examination of the data summary in Table VIII, it is apparent that due to the randomness of the data collection (dictated by the complexities of sample collection, analytical methods and number of variables), it was necessary to apply methods of statistical analysis. Therefore, the laboratory data was subjected to a correlation analysis to determine the relationship of each parameter and its significance to the electrode potential. Linear and curvilinear (exponential) correlation programs were written in Fortran IV language and the data analyzed on an IBM 360 and IBM 1130 computer. The output from the program includes the correlation coefficient, the fiducial limit (± one standard error) and the graphical presentation based on a separate plotting subroutine.

Linear correlation between the electrode potential and BOD of the sewage is shown in Figure 13. The constants for the regression equation were also printed out by the computer and the linear correlation coefficient was found to be 0.873 which is significant. The computer plot of an exponential relationship between potential and BOD is shown in Figure 14, which also shows significant correlation between the two parameters.

Linear correlation between electrode potential and sulfides is shown in Figure 15. The correlation coefficient is 0.896 which is also significant. For comparison, the computer plot of an exponential relationship between potential and sulfides is shown in Figure 16 which is also of interest.

Examination of the relationship between electrode potential and total phosphorous concentration (by the persulfate digestion method) also resulted in a significant correlation, $r = 0.893$, as shown in Figure 17.

TABLE VIII - SUMMARY TABULATION OF DATA FROM POTENTIAL STUDY (FWPCA)

Sewage Sample Date 1969	Analysis Date 1969	Temperature (°C)	ORP(a) (mv)	DO (mg/l)	BOD (mg/l)	COD (mg/l)	Residue			Ammonia (mg/l)	NO_3^- (mg/l)	Total Organic (mg/l)	Total Phosporous (persulfate) (mg/l)	Cl^- (mg/l)	$S^=$ (mg/l)	pH	Settle-able Matter (ml/l)	Grease (mg/l)	Coliform 100/ml	
							Total Solids (mg/l)	Fixed Solids (mg/l)	Volatile Solids (mg/l)										MPN	Fecal
7-23	7-24	25	+ 31		355															
	7-29	25	+ 80		52															
	7-29	25	0			77														
7-25	8-19	25	- 15			379					2.6									
	8-20	25	+ 56		50	102														
	8-29	25	-220		225	625									2.9	8.02				
	9-03	25	-228												4.8	8.02				
	9-08	25	-236	0.0		349	888	362	526						5.4	8.02				
	9-10	25	-240	0.0			721	277	444						6.1	8.02				
	9-11	25	-248	0.0	138	283					6.5				0.5	8.02				
8-27	9-22	25	-225	0.0		206	848	356	492							7.52	200			
	9-23	25	-231		99	191					5.6				3.3	7.54				
	9-24	25	-235				1056	738	318											
	9-26	25	-230	0.0							6.2						410			
	9-29	25	-210	0.0		75								20.5	<1.0					
	9-30	25	-190		49								7.2					7.7		
	10-02	25	-112														450			
	10-03	25	-125			32	1048	312	737					18.5			445			
	10-06	25	-150										6.4		<1.0			7.8		
	10-08	25	-110		20															
10-16	10-23	20	-329	0.0	312	568	857	358	498					53.4			250			
	10-24	20	-300	0.0	220	480					6.2		5.6							
	10-26	20	-150		107		927	350	577						4.35			8.8		
	10-27	20	-148	1.1		231							5.2	33			440	8.7		
	10-29	20	- 59		62	114	1068	439	626		7.0									
10-31	11-03	20	-258		290									31.7	7.55			9.4		
	11-12	20	-382												17.2					
	11-18	20	-192	1.8	90										8.7					
11-19	11-21	20	- 72	3.8	107										2.4					
12-02	12-02	20	-299		252		838	324	514							6.90	300			
	12-03	20	-278	0.0		464				19.0				43.2		6.07				
	12-05	20	-203	0.6	165						7.4		7.6			7.11	455	10.5		
	12-06	20	-182							22.4		27.8			5.4					
	12-08	20	- 93		49		953	417	536				6.7	41.1		7.20				
1970																				
1-07	1-07	20	-205	0.0	221	451	846	410	436					160.9	4.8		150			
	1-08	20	-208							16.7	6.5		7.6				210	9.7	1.1x10^8	1.1x10^8
	1-09	20	-180	0.0	156						7.2		7.2	240.9	3.7				2.4x10^8	1.1x10^8
	1-10	20	-150				1083	506	577			28.4					350	10.5		
	1-12	20	-111	1.2	99	220								150.4	1.3		520		2.4x10^8	9.3x10^6
	1-13	20	- 75	2.1						21.8	7.85	25.7	5.35	142.5					2.4x10^8	4.6x10^6
	1-14	20	- 70		33	102							5.0		<1.0		650	7.25	2.4x10^8	4.3x10^6
	1-19	20	- 58	2.3	31		1039	464	575					141.9	<1.0				1.1x10^8	4.6x10^6
	1-20	20	- 37	2.4		75					7.9		5.7	140.3			550	8.25		
	1-21	20	- 34	2.5		70	1041	469	572	20.45		23.85		145.5						
2-05	2-05	20	+118	3.5	109	207					2.5		3.7	106.8		6.8				
	2-06	20	+191	4.2	68	132	476	222	255	7.0		10.35		112.0		6.8	70			
	2-09	20	+230	4.8		86					2.75		3.65	100.8		6.8	100			

(a) Fischer and Porter cell.

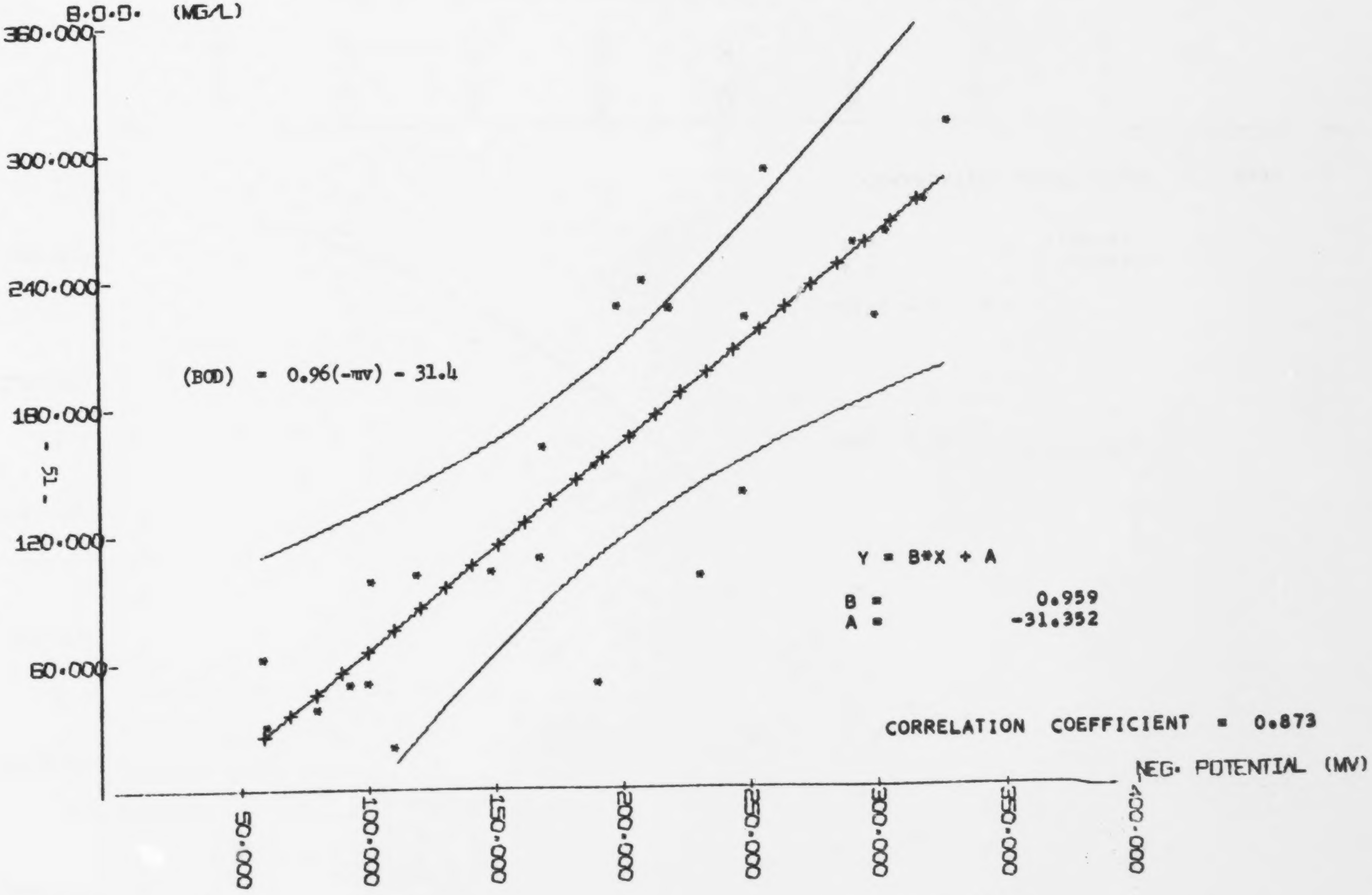


Figure 13 Linear Correlation of Electrode Potential with BOD

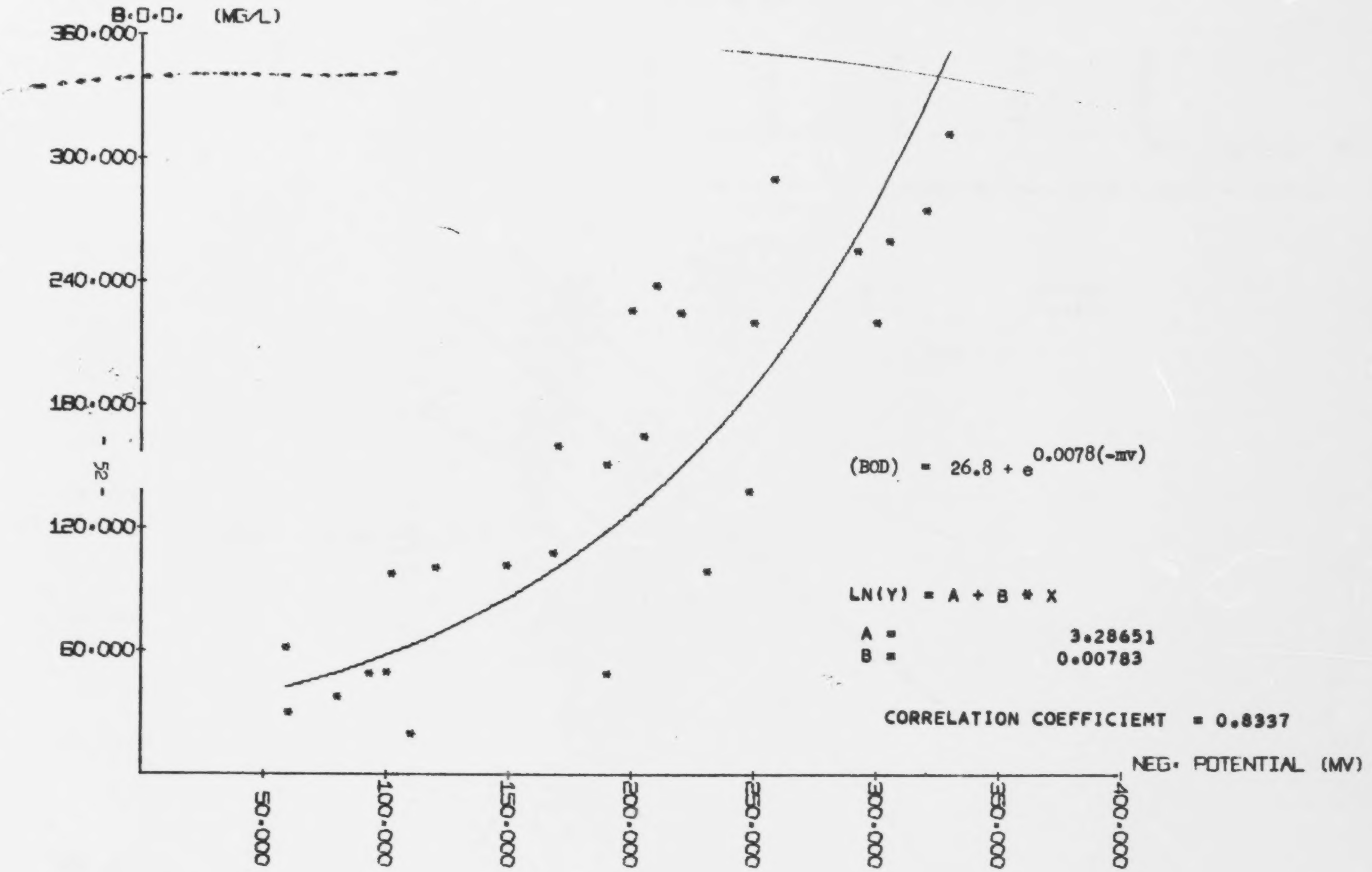


Figure 14 Exponential Correlation of Electrode Potential with BOD

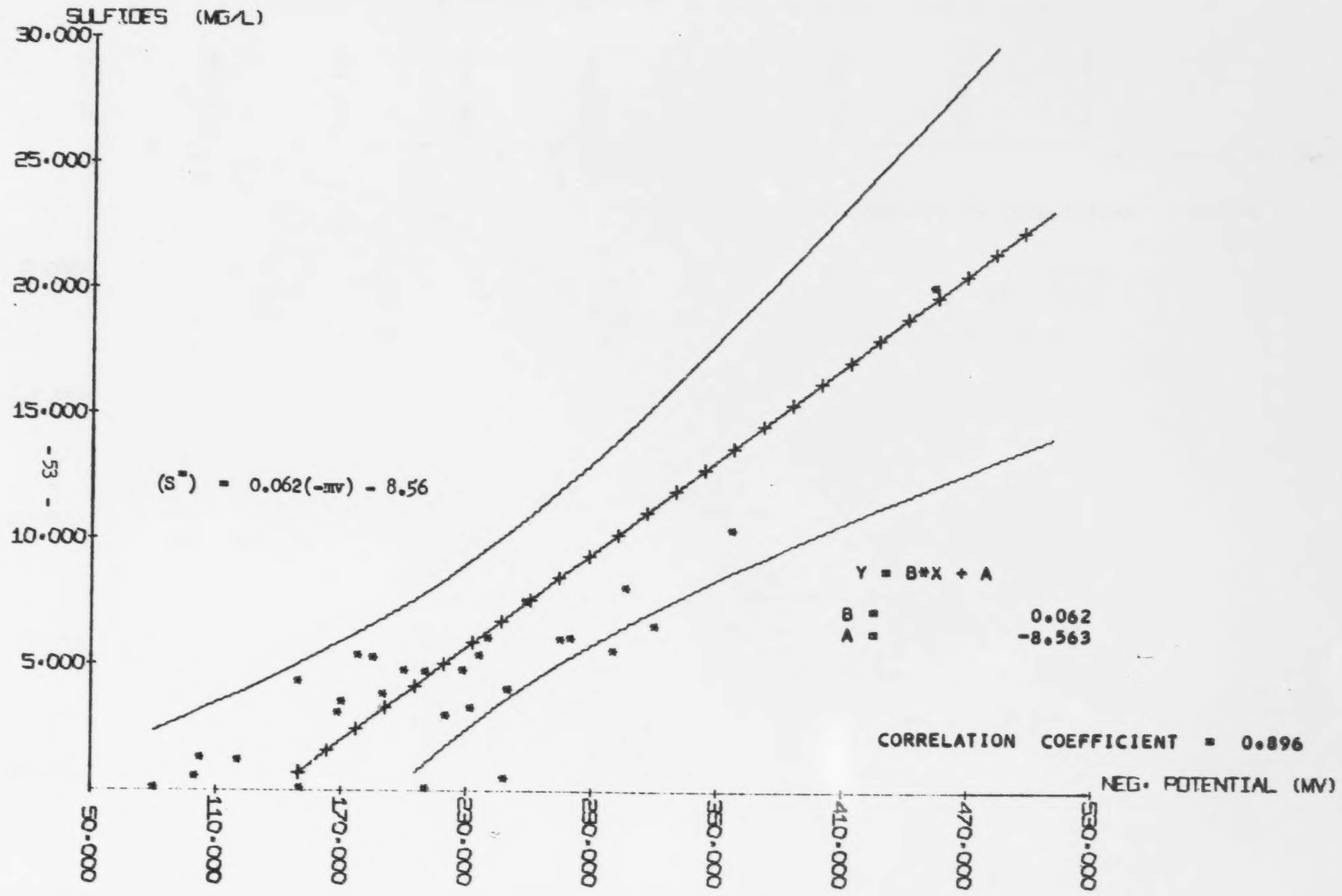


Figure 15 Linear Correlation of Electrode Potential with Sulfides

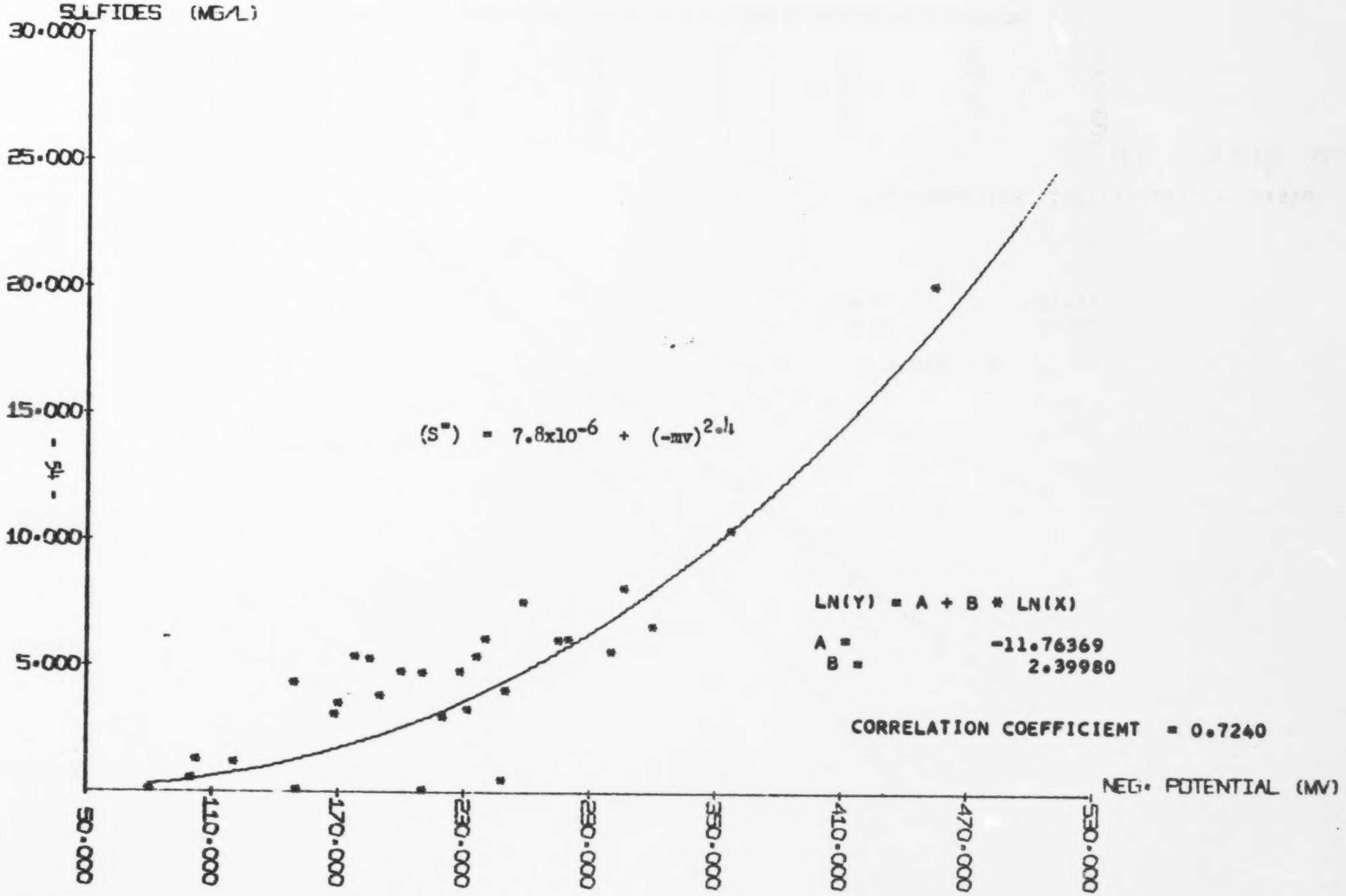


Figure 16 Exponential Correlation of Electrode Potential with Sulfides

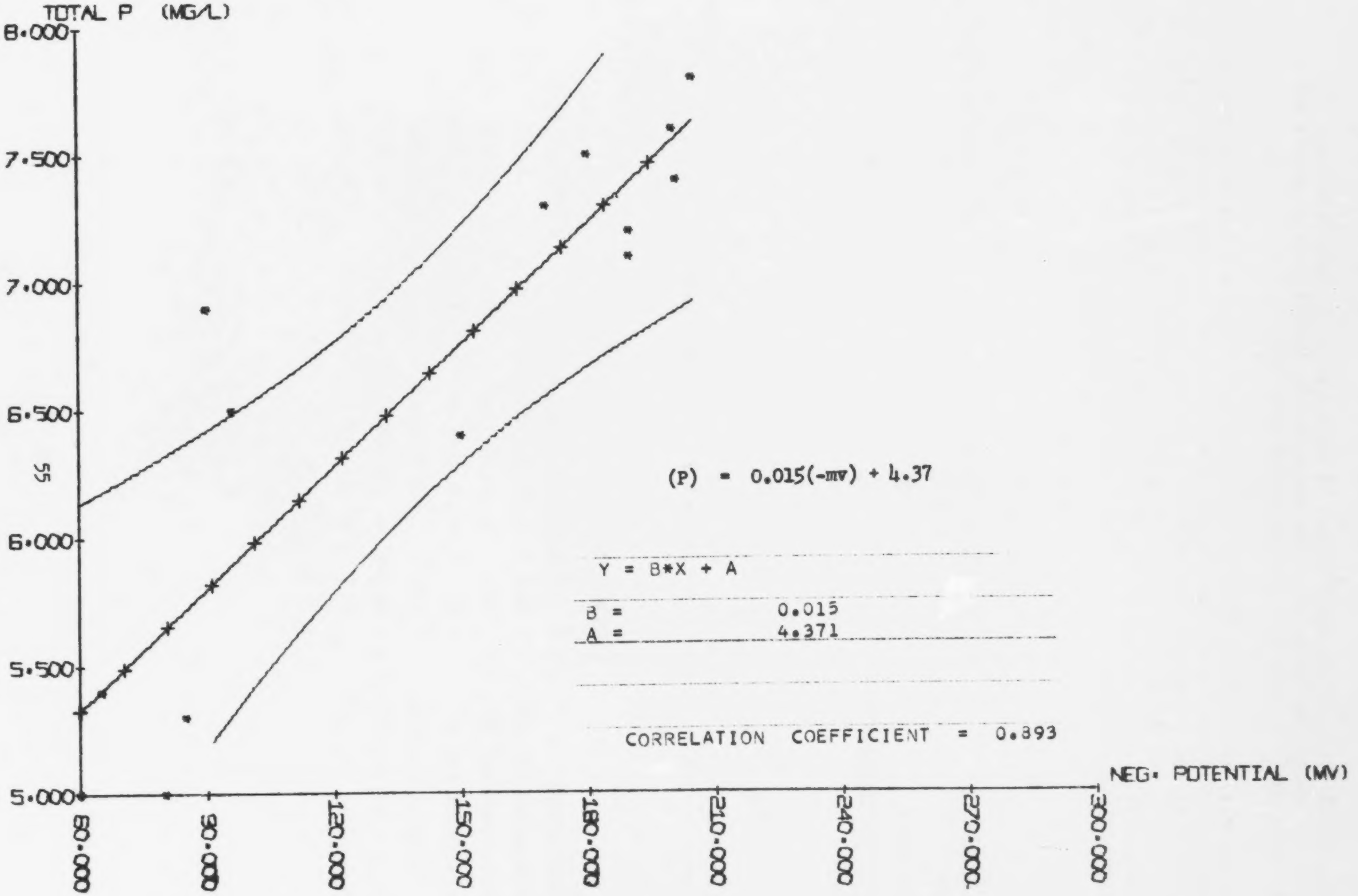


Figure 17 Correlation of Electrode Potential with Total Phosphorous

The results of linear correlation between electrode potential and the COD are shown in Figure 18. The correlation coefficient is 0.852 which is comparable to the 0.873 value found with BOD.

Similarly, the correlations of potential with nitrates and chlorides are shown in Figures 19 and 20. Significant correlation between NO_3-N and potential was found but not between chlorides and the potential. This result is not unexpected since high concentrations of chlorides do not participate in biochemical degradation reactions. A summary of the correlation coefficients is shown in Table IX.

TABLE IX

Parameter	Correlation Coefficients Linear Correlation	Curvilinear (Exponential) Correlation
BOD	0.873	0.834
Sulfides	0.896	0.724
Total Phosphorous	0.893	0.897
COD	0.852	0.726
Nitrates	-0.807	-0.784
Chlorides	-0.225	-0.213

For additional information, the equations of best fit and their correlation coefficients for these five parameters are given below:

TABLE X

Summary of Correlation Analysis

Parameters	Equation of Best Fit	Correlation Coefficient
Potential vs. BOD	BOD = 0.96(-mv) - 31.4	0.873
Potential vs. $S^=$	$S^=$ = 0.062(-mv) - 8.56	0.896
Potential vs. P	P = 0.015(-mv) + 4.37	0.893
Potential vs. COD	COD = 1.64(-mv) - 13.1	0.852
Potential vs. NO_3-N	NO_3-N = -0.0066(-mv) + 7.93	-0.807
Potential vs. Cl^-	Cl^- = -0.22(-mv) + 138.7	-0.225

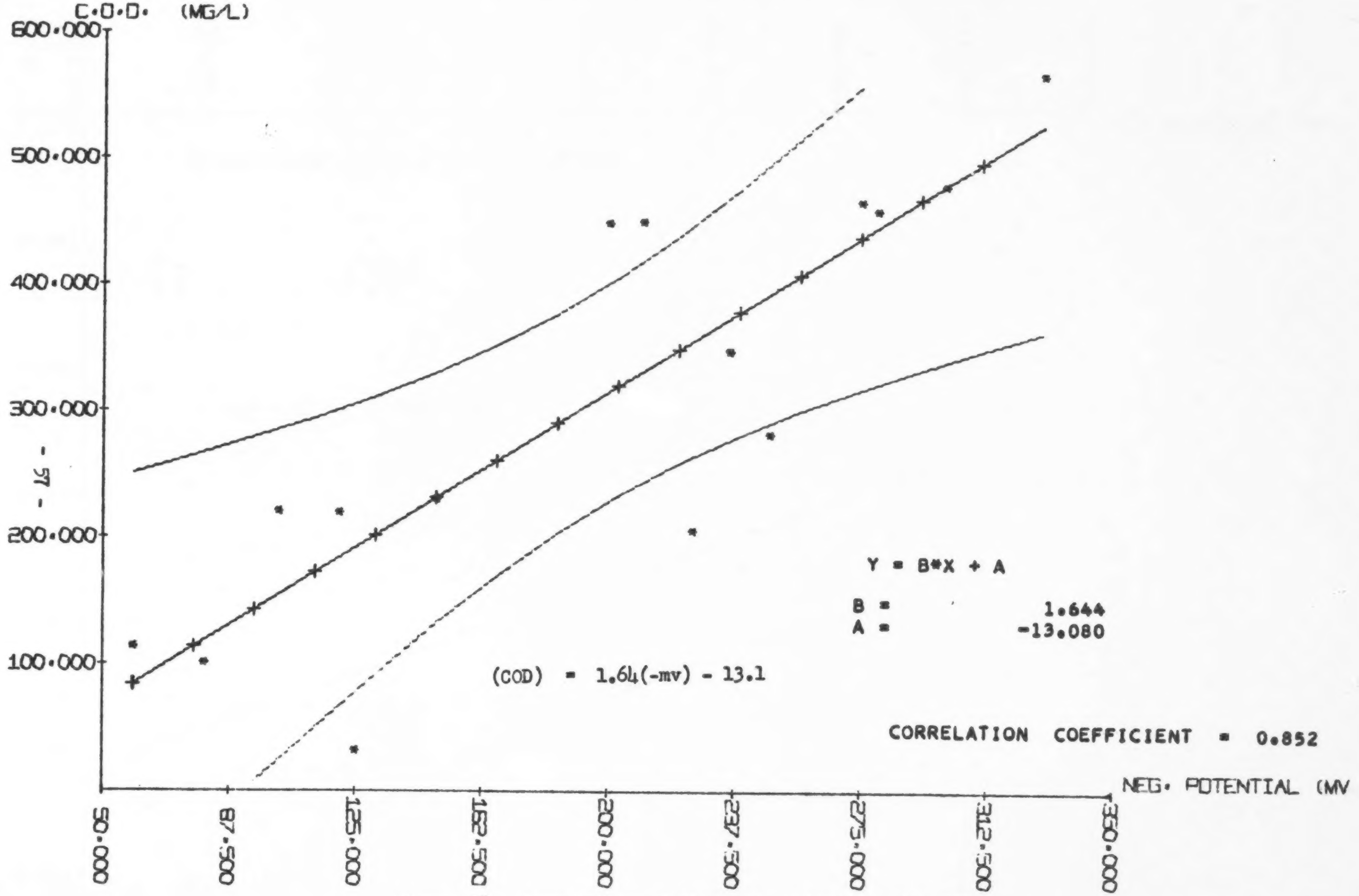


Figure 18 Correlation of Electrode Potential with COD

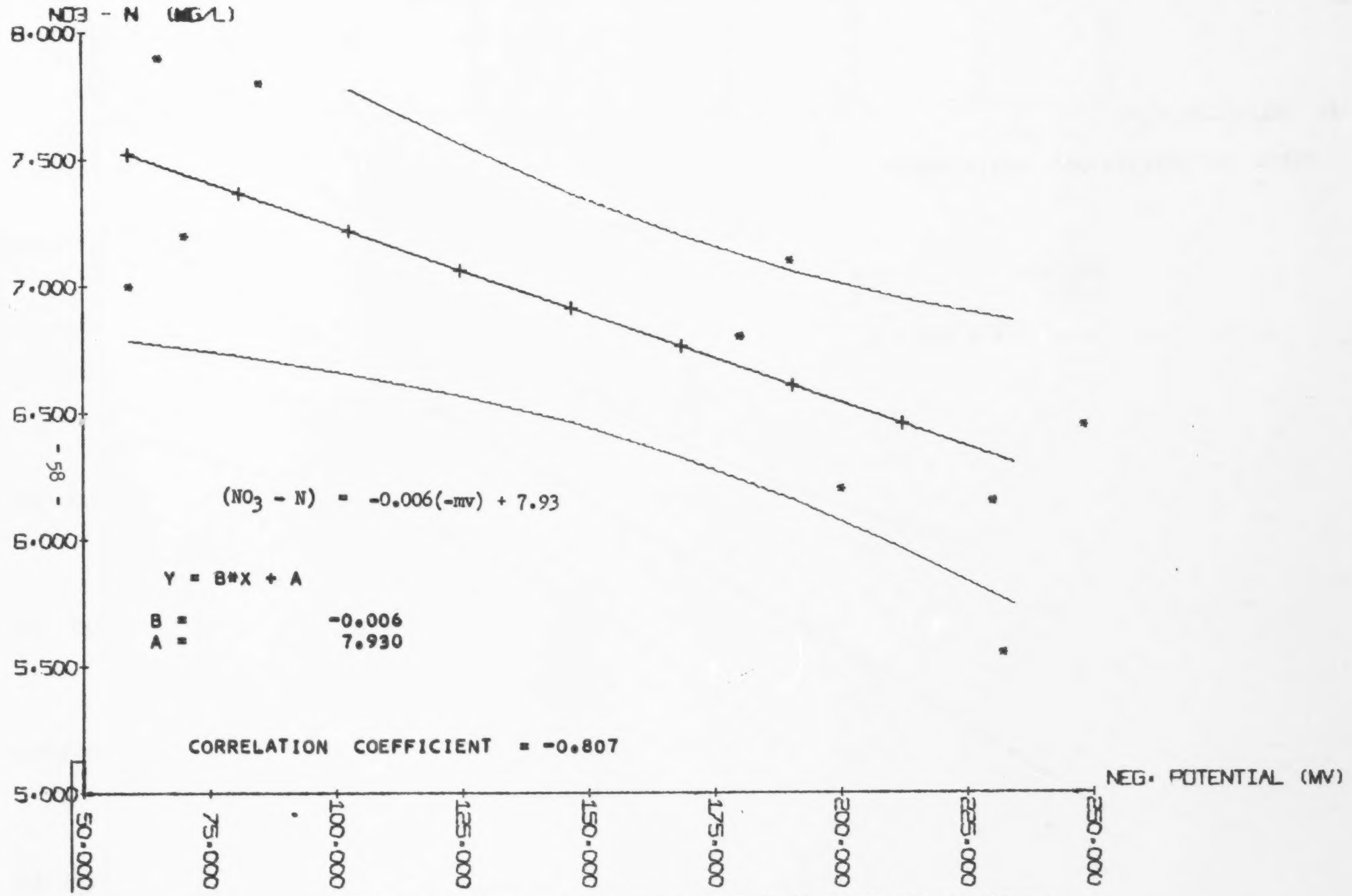


Figure 19 Correlation of Electrode Potential with Nitrate Nitrogen

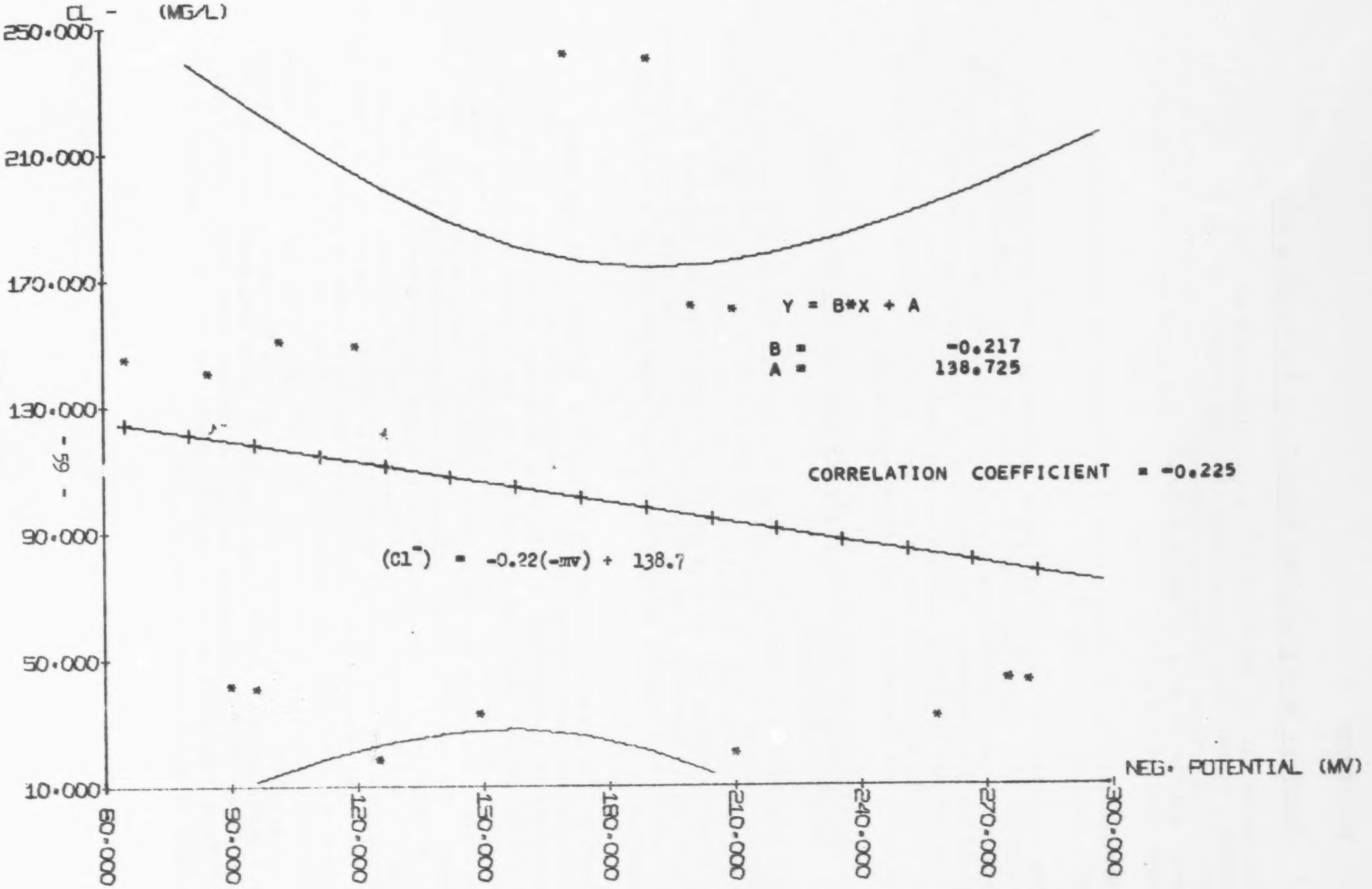


Figure 20 Correlation of Electrode Potential with Chlorides

VIII. DISCUSSION

A. Response, Sensitivity and Stability of Electrode System

As the result of these laboratory investigations with weak to strong sewage, it has been demonstrated that the response of certain potential measuring systems can be instantaneous. Not all systems perform equally well and the conditions for measurement are important, including proper electrode maintenance.

The sensitivity of these systems is excellent, a reproducibility of 1 to 2 mv can be expected.

The stability of several electrode systems has been investigated and found to vary among these systems. The stability of the immersion type system is questionable in a prototype installation because of electrode polarization. However, the stability of the potential obtained with flow-through electrode systems is excellent (no polarization in the presence of strong sewage solids and normal grease concentrations), provided the flow through the cell is maintained continuously.

B. Sensitivity of Potential to the Strength of Untreated Sewage and Waste Effluents

The sensitivity of the flow-through Fischer and Porter cell to various sewages varying from 109 ppm to 312 ppm B.O.D. and from 476 ppm to 857 ppm Total Solids has been demonstrated in the laboratory. This data is limited to the extent of nine different sewage samples analyzed from July 1969 to February 1970. Further substantiating work in the laboratory for additional support data is necessary, supplemented by a field demonstration.

Based on the present laboratory data, it is evident that the redox potential is sensitive to the B.O.D. concentration ($r = 0.85$). The potential is insensitive to chlorides which may be expected since chlorides do not participate generally in the biochemical reactions or determine the nature of biotic microenvironments. A relatively high negative correlation of the nitrates with the negative potential was found. The negative correlation simply indicates that the higher the NO_3-N concentration, or the more stabilized the substrate, the less negative the potential would be expected. The relatively high degree of correlation was not expected but is interesting. Similarly, the correlation of the total phosphorous concentration (as determined by persulfate digestion) with electrode potential is significant ($r = 0.89$) and lends additional emphasis to the concept that the potential will also be useful in controlling the discharges from urban runoff and agricultural drainage from storm sewers. Further experimental work is indicated and should be carried out in the laboratory during the second year, concurrently with the field demonstration in a combined sewer, as has been suggested in the renewal proposal dated January 26, 1970.

C. Effect of Interfering Substances or Predominant Oxidants; Phosphate Buffer Poising

To determine the transient effect of interfering substances on the electrode potential, several experiments were carried out. On several occasions, highly anaerobic or stale sewage was aerated and the potential recorded. An instantaneous and significant rise was observed in each case. In addition to analyzing for sulfides and measuring the potential, the sulfide concentration in the substrate was also artificially increased in the form of Na_2S and the effect on the potential noted (see data shown in Table VII).

Thus, the electrode potential system was found to respond immediately to the presence or sudden change in concentration of an oxidant or reductant. Further work with other oxidants and reductants should be conducted to further substantiate these findings before they can be generalized.

As already discussed, the total phosphorous concentration has been found to correlate to a high degree with the electrode potential. Thus, the presence of nutrients (at least phosphorous) appears to be amenable to electrode potential detection rather than interfere with this method for controlling harmful discharges.

To improve the poising of the substrate medium for a more stable measurement, the addition of phosphate buffer(*) to various substrates was examined in the presence of sulfides. A sample of distilled water to which concentrations of up to 50 ppm of buffer had been added showed the negative potential to increase by about 100 mv as the concentration of $S^=$ increased from 5 to 50 ppm. When the same concentrations of sulfide were added to a sample of phosphate buffer the potential increased only 50 mv. Thus, the buffer appears to have improved the poising of the potential over the distilled water.

A similar set of experiments was carried out on sewage to determine the degree of poising achieved with phosphate buffer. A sample of sewage to which concentrations up to 50 ppm of $S^=$ had been added, showed the negative potential to increase by about 50 mv as the concentration of $S^=$ increased from 5 to 50 ppm. When the same concentrations of $S^=$ were added to a sample of sewage, to which 10% by volume of phosphate buffer had been added, the potential remained unchanged (-240 mv) until the maximum of 50 ppm of $S^=$ were added, at which time the negative potential increased by 5 mv (-245 mv). These experiments show that (i) distilled water is a poorly poised system, (ii) domestic sewage is a more poised system, (iii) the addition of phosphate buffer to sewage tends to completely poise the system (even in the presence of an interfering system, i.e. a strong reductant). From these experiments, it would appear that the potential measurement of dilute sewages (such as combined sewage and stormwater) may be accomplished withoug the addition of a poising agent, even in the case of nominal concentrations of a predominant reductant. However, in cases where particularly strong reductants are present in high concentrations the addition of a poising agent may be beneficial. Further exploration of these concepts is necessary before any definite statements can be supported as valid.

(*) Phosphate buffer as specified for the B.O.D. procedure in Standard Methods.

D. Zones of Potentials when Layering Occurs and Possible Compensation for Such Events

It is possible to visualize a free-flowing sewer as being composed of two zones of potential. The body of the flow may exhibit even a positive potential, E_h, in the presence of oxygen diffusing into this flow. However, the slime growths along the wall will exhibit negative potentials as in the presence of S. desulfuricans. These organisms exist in large quantities only in potential ranges of -200 mv to -300 mv, indicating highly anaerobic conditions generally accompanied by an active generation of sulfides. Thus, under certain circumstances, the existence of two zones of potential in a flowing sewer is possible.

However, the potential method investigated herein is concerned with controlling the quanity of the flow that is being discharged. The discharge from a sewerage system will reflect the conditions of the system, the dry-weather and wet-weather flows in the case of combined sewers and the type of storm. If the initial slug contains slimes scoured from the wall (and this may well be the case after a prolonged drought) or if the system has small slopes, the solubility of sulfides is such that they will exert their influence on the potential almost instantaneously. After the initial scouring of the sewer barrel, if the storm subsides or if the system carries a fresh sewage, there will be generally no significant concentration of sulfides and the potential will be less negative or may be positive and the flow may be discharged directly. In some instances it may be necessary to install flow-through cells at different levels and to telemeter an integrated signal to the flow control device.

E. Effect of Different Cell Systems on the Response

Both Beckman and Leeds and Northrup immersion electrodes were used to measure the potential of untreated sewage, but these systems do have the problem of electrode polarization due to the presence of grease and slime growths. Thus, they are rendered insensitive in a relatively short period of time.

Investigation of the non-fouling reference electrode (Cu plate) together with a thin-film Pt-encapsulated electrode system(a) showed that the signal drifted when measuring sewage potentials, although earlier calibration experiments (see Table VIO had been most encouraging. However, during the experimentation with sewage the Cu-Pt electrode system was found to be relatively insensitive and unstable. Therefore, evaluation of this immersion electrode system was abandoned during October 1969.

The Ag, AgCl-Pt flow-through electrode system(b), used throughout most of these investigations, has been quite sensitive to variable potentials, registered changes instantaneously and showed excellent stability without polarization. Maintenance of the electrode system has been negligible in spite of the fact that potentials varying from +200 mv to -350 mv have been recorded and sewages with concentrations up to 30 ppm of total sulfides were measured. The cleaning of the flow-through cell assembly can be readily accomplished with a test tube brush and plenty of water. In especially difficult cases, after prolonged operation of the cell, it may be necessary to use a dilute (1.5%) solution of HCl to rejuvenate the noble metal electrode.

(a) Manufactured by Delta Scientific Corporation, Lindenhurst, New York.
(b) Manufactured by Fischer and Porter Company, Warminster, Pennsylvania.

In spite of the successfully demonstrated response, especially with the 3/8-in. diameter flow-through cells, the instantaneous changes in the wastewater quality from combined and storm sewers may reflect in highly variable potentials. Therefore, the mv signal may have to be integrated with a definite time constant before telemetering the signal to operate the flow control device (gate valve or equivalent). From the above experiments, it appears that a meaningful modulation of the flow can be achieved.

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~~The objective was to investigate~~ the effectiveness was investigated of electrode potential measurements to modulate discharges from combined and storm sewer overflows to reduce stream and estuarine pollution. Studies included varying the composition of sewage, flow rate and examining the tendency to polarize or coat the electrodes under actual flow conditions. The analysis of experimental results shows a high degree of correlation between the electrode potential of the sewage and its strength. Linear correlation coefficients between electrode potential were determined for BOD, COD, Sulfides, total phosphorus, nitrates, and chlorides.

It was demonstrated that the potential will be more negative the greater the $S^=$ concentration, except when a small amount of DO is present which exerts an attenuating influence. Flows carrying substantial concentrations of reducing substances with a detrimental impact on the dissolved oxygen reservoir of any receiving waters must be kept from exerting their damaging influence on bathing beaches, tidal estuaries and other water resources. Controlling the flow from outfalls by the electrode potential should significantly help to minimize such insults to the environment.

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